PH.D THESIS

REE-bearing carbonate systems at high pressure: an experimental study

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Ai miei genitori, da sempre esempio di vita. Esemplari lavoratori che, con il loro instancabile sostegno morale ed economico, hanno costantemente sostenuto i miei progetti, contribuendo alla mia formazione professionale.

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Abstract

REE-bearing carbonate systems at high pressure: an experimental study

Carbonatites are important sources of Rare Earth Elements (REE). REE mainly reside in Ca-bearing phases carbonates, apatites, Ca-Nb oxides, Ca-silicates and in accessory phases such as monazite, burbankite, bastnäsite. At liquid phases, carbonate melts display remarkable physical properties. In particular, carbon-rich and silica-poor melts, i.e. transitional melts, are efficient metasomatizing agents of carbon between the mantle and the crust.

This study focuses on two main issues: I) the effect of REE such as La and Y on the structure and melting behavior of transitional carbonate-silicate melts, which has been investigated in simple model with variable $CaCO_3$:SiO_2 ratio at 1 GPa; and II) the stability and mineral physics of REE-bearing carbonates at high pressure, in particular of La-burbankite.

Few experimental works have explored phase relations, structure and the role of REE in carbonate-rich melts. The typical unquenchable nature of carbon-rich melts makes for a difficult, determination of the structure of carbon-rich glasses. Wyllie and Jones (1986) synthesized a REE-bearing carbonatite glass in a series of experiments performed in the system $CaO–CaF_2–BaSO_4–CO_2–H_2O–La(OH)_3$ using a composition similar to carbonatites ore deposits in Mountain Pass (California). At 0.1 GPa the investigated carbonatite composition starts to melt at temperatures as low as 550°C. As today, there are no data available regarding melting behavior, structural properties of melts, and the stability of REE-bearing phases in model system of hydrous carbon-rich low silica. Furthermore, although in alkali free systems a complete miscibility between silicate and carbonate liquids is expected, the compositional threshold at which carbonate-silicate liquids might form a glass, i.e. are quenchable, is still scarcely explored in simple model systems. In this study, I investigated i) how viable is the quenching of a carbon-rich melt as a function of the bulk SiO_2:$CaCO_3$ ratio, ii) the structure of these glasses, iii) and the role of REE in the molecular structure(La, Y). I also determined the CO_2 solubility in transitional melts by micro-Raman spectroscopy. Single stage and end-loaded piston cylinder experiments have been performed at 1 GPa in two model systems: $CaO–SiO_2–La_2O_3–H_2O–CO_2$ in the range 700–1250°C, and $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ in the range 1200–1250°C. The starting materials were prepared as a powder mixture of $La_2(CO_3)_3$ or La_2O_3 or Y_2O_3 and amorphous SiO_2 and $CaCO_3$ with approximately 5-10 wt.% of H_2O. Different bulk compositions with different SiO_2:$CaCO_3$ ratio have been considered. Run products were characterized by backscattered electrons images (BSE), X-ray diffractometry, micro-Raman spectroscopy, nuclear magnetic resonance (NMR) of selected experiments, and chemically analyzed by electron microprobe. At subsolidus conditions (T < 1000°C), all bulk compositions in $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system contain calcite and quartz coexisting with a Ca-La silicate phase with an apatite-type structure of general formula between $La_3Ca_2(Si_3O_{12})OH$ and $La_4Ca(Si_3O_{12})O$. Liquidus conditions have been observed in runs on

bulk compositions with $SiO_2:CaCO_3$ = 0.28–1.4 at T >1150°C for both investigated systems. Homogeneous quenched glasses have been retrieved for composition with up to $SiO_2:CaCO_3$=0.28 ratio, whereas at lower ratio (0.12) dendritic textures are visible. Deconvolution of Raman spectra of glasses reveal a CO_2 content up to 20.40% in the CaO–SiO_2–La_2O_3–CO_2–H_2O system and up to 10.80% in the CaO–SiO_2–Y_2O_3–CO_2–H_2O system classifying the melts as carbonate-silicate transitional melt.

While studiyng the behavior of Ca-rich carbonatitic hydrous glasses with REE, we also investigated the influence on the REE distribution of an alkaline carbonate, burbankite $[(Na,Ca)_3(Sr,Ba,Ce,REE)_3(CO_3)_5]$, at upper mantle conditions. Recently, the alkaline-carbonate system has been observed at High Pressure and High Temperature (HP-HT) by Shatzky et al., (2016); they found a new class of Ca-rich alkaline-alkaline earth carbonates and burbankite with the latter being abundantely presents in carbonatites that constitutes important ore concentrations of strategic metals, including Nb and REE elements on Earth's surface. A La rich burbankite $[Na_3Ca_2La(CO_3)_5]$ was synthesized at 5 GPa and 1000°C, to scope out the possibility that REE can enter the structure of this carbonate also at upper mantle conditions. Furthermore, the elastic properties of the synthesized La-burbankite have been determined by in-situ HP and HT single crystal X-ray diffraction measurements at synchrotron facilities using a diamond-anvil cell for HP experiments and a quartz-glass capillary for the HT experiments. The determination of these thermoelastic parameters allowed to calculate the possible density of this phase at upper mantle conditions, that is ca. 3.2 g/cm^3 at 5.5–6.0 GPa and 900–1000°C. Results suggest that potentially the La-burbankite could fractionate at HP and HT from a carbonatitic melt, because the latter has a lower density (ca. 2.1-3.1 g/cm^3) and may constitute a REEs reservoir at upper mantle conditions.

Introduction

Carbon in the Earth system and carbonatites

Carbon, in the form of CO_2 or carbonate, is the second most abundant volatile component in magmatic systems. Although its concentration is typically lower than water (Carroll & Holloway, 1994), experimental data (Wallace & Green, 1988; Yaxley & Brey, 2004; Dasgupta & Hirschmann, 2006, 2010) and field-based evidence - e.g. the mineralogy and geochemistry of xenoliths from alkali basalts, inclusions in diamonds and in mantle minerals in garnet peridotites xenoliths - suggest that primary carbonate melts exist in the upper Earth mantle.

Several experimental studies on silicate-carbonate systems have been undertaken during the past four decades, and the results have been used to speculate on the origin of carbonatite magmas.

Three petrogenetic models (Figure 1) have been proposed for the generation of carbonatitic magmas. Carbonate melts may evolve from:

1. separation of a carbonatite from a silicate melt by liquid immiscibility (Lee & Wyllie, 1997; Veksler et al., 1998, 2012; Brooker & Kjarsgaard, 2011), which has implications for the origin of REE mineralization;
2. formation as evolved melts through extensive fractional crystallization from a CO_2-bearing silicate liquid (i.e. kimberlites) (Watkinson & Wyllie, 1971; Nielsen & Veksler, 2002; Ulmer & Sweeney, 2002);
3. derivation as primary liquids by low-degree partial melting (generally < 1%) of a carbonated mantle peridotite or eclogite (Wallace & Green, 1988; Dalton & Wood, 1993; Harmer & Gittins, 1998; Brey et al., 2008; Dasgupta et al., 2009; Hammouda et al., 2009, Tumiati et al., 2013).

Figure 1 - Petrogenesis of carbonatites. CM—carbonate melts; SM—silicate melts; ASR—alkaline silicate rocks (adapted from Ye et al., 87).

Low degree partial melting generates carbon-rich and typically silica-poor melts (e.g. Wyllie & Huang, 1976; Eggler, 1978; Dalton & Presnall, 1998; Gudfinnsson & Presnall, 2005; Dasgupta & Hirschmann, 2006 and Dasgupta et al., 2013; Massuyeau et al., 2015). These transitional melts between pure carbonatite and silicate composition (between 10 and 40 wt.% SiO_2) are inferred to be widespread in the Earth mantle and can contain several tens of wt.% of CO_2 (Brey & Green, 1976; Moussallam et al., 2014).

Carbon-rich and typically silica-poor melts are characterized by extremely low densities and viscosities (Weast & Astle 1980): they are highly mobile, able to wet the surface of silicate minerals, to rapidly leave the source, and migrate towards the crust even at low melt fractions. As a result, they are considered potential efficient metasomatized agents (Grégoire et al., 2000; Kamenetsky et al., 2004), suitable to transport significant amount of incompatible major and minor elements, together with volatiles such as CO_2, H_2O, halogens and sulfur, efficiently contributing to fluxes of carbon between reservoirs in deep and shallow Earth.

Carbonate melts are also important source of ore-forming minerals, as host of REE, having the highest REE concentrations of any igneous rocks (Chakhmouradian & Zaitsev, 2012) and thus have been long exploited. In recent decades, REE have been considered strategic metals and their economic and technological importance has grown: they are a key component in the manufacturing of modern technologies with a multitude of application, and are among the most critical of all raw materials. REE are widely used in hybrid vehicles, rechargeable batteries, mobile phones, flat screen display panels and electronic products, with a special focus on sustainability. The glass industry is the main consumer of REE raw materials, used for the fabrication of optical glasses (Goonan, 2011).

The genesis of carbonatite-related REE deposits is still under debate; ore-forming elements are mainly sourced from primitive mantle, with possible contribution of crustal materials that carry a large amount of REE and it is generally believed that the carbonatite magma is originated from the low-degree partial melting of rich H_2O and CO_2 mantle. Carbonate melts show a high solubility of elements considered rare in silicate magmas, with the highest known melt capacities for dissolving water and other volatile species at crustal pressures (Jones et al., 2013).

The physical properties of carbonate-silicate transitional melts affect their behavior as metasomatizing agents and REE carrier from the source toward the crust. These transport properties are strongly related to the molecular structure of such melts; however, investigations in the structure of carbonate-bearing are limited compared to the structure of silicate melts.

As liquids, carbonate melts are ionic liquids, and composed of discrete, non-polymerized ions (Zarzycki, 1962). Transitional melts are combined by the ionic structure of carbonatite and the polymerized structure typical of silicate melts (Mysen, 1983). While polymerized melts are easily quenchable, carbon-rich melts are also known to be unquenchable (Genge et al., 1995); this feature reduces a lot the knowledge we have on their properties.

The mineralogy and the stability of REE-bearing carbonates at mantle conditions is also of great relevance: about 270 REE-bearing minerals have been identified, and they can be

divided into three groups. The first includes primary magmatic minerals formed by crystallization from carbonatite melts; the second type is of hydrothermal-metasomatic origin and the third group is linked to supergene processes. Among REE-minerals, the carbonates constitute a relevant fraction. Furthermore, an important (third) group of alkaline carbonates containing REE can be primary phases in equilibrium with the carbonatite liquid.

Aims of this work

This thesis deals with carbonatite systems following two main issues: I) the effect of REE, such as La and Y, in the structure and melting behavior of transitional carbonate-silicate melts investigated through simple model systems with variable $CaCO_3:SiO_2$ ratio at 1 GPa; II) evaluate the stability and mineral physics of REE-bearing carbonates at high pressure, in particular of burbankite $[(Na,Ca)_3(Sr,Ba,Ce,REE)_3(CO_3)_5]$.

I)   The $REE–CaO–SiO_2–H_2O–CO_2$ system: the role of La and Y in the melting behavior and structure

Experimental studies of carbonatite systems have been undertaken since the 1960s to prove the igneous origin of carbonatites.

Different and complex systems have been investigated to study chemical and physical properties of carbonatite melts and the association with alkali rocks and kimberlite to unravel the immiscibility relations between silicate and carbon bearing melts (e.g. Van Groos & Wyllie, 1966, 1968, 1973; Kjarsgaard & Hamilton, 1988, 1989; Brooker & Hamilton, 1990; Lee & Wyllie, 1994, 1996, 1997; Martin et al., 2013).

Many studies and experimental evidence confirm that carbonatites magmas separate from silicate by immiscibility across a large range of composition (Le Baas 1977; Freestone & Hamilton 1980; Macdonald 1993). However, little is known about the structure of transitional melts, and on the solubility of CO_2 in these low silica carbon rich compositions. The simple system $CaO–SiO_2–CO_2–H_2O$ is considered to be the simplest and it has been investigated by Boettcher and Wyllie 1969 who demonstrated that fractional crystallization produces carbonate melts from liquidus undersaturated in silica. The present study will add complexity to the system adding REE to evaluate the effect of La and Y in melting relation, quenchability, structure and physical properties.

Phase relations, structure and the role of REE in carbonate-rich melts are so far poorly known. The only experimental work is based on the complex system $La(OH)_3–Ca(OH)_2–CaCO_3–CaF–BaSO_4$ (Jones & Wyllie,1983). The authors investigated a composition similar to typical carbonatites ore deposits (Mountain Pass, California). Although this is the only study that succeeded in quenching REE-bearing carbonate melts, the molecular structure is still scarcely investigated: in 1983, Jones and Wyllie found the only carbonate REE bearing glasses known at crustal conditions at 0.1 GPa able to reproduce phase relations in highly

fractionated systems. This experimental study demonstrates that bastnaesite (La, Ce, Y) CO_3F, a REE carbonate present in up of 15% vol in Mountain Pass – California ore body, can precipitate from a carbonatite melt.

Genge et al., (1994) investigated the same La-bearing system $La(OH)_3$–$Ca(OH)_2$–$CaCO_3$–CaF–$BaSO_4$ by Raman and infrared spectroscopy to better constrain the local structure of these glasses and natural carbonatite magmas.

In this study, the distribution of REE, in particular La and Y (representing heavy and light rare earth elements), in low-silica carbonate system will be experimentally investigated at 1 GPa in a free-alkali hydrous system at different SiO_2:$CaCO_3$ ratio.

This research will also contribute to find out the CO_2 solubility in transitional melts.

The CO_2 behavior in silicate melt is well-known thanks to numerous experimental works accomplished in the last decades (Blank & Brooker, 1994; Thibault & Holloway, 1994; Morizet et al., 2002). Thus, investigating the relationship between CO_2 and REE in low silica carbon-rich melts might be significant.

II)   The stability and mineral physics of REE-bearing carbonates, in particular of burbankite, is investigated by synthesis at 5 GPa and *in-situ* high-pressure synchrotron X-ray diffraction.

Studies on REE-bearing alkali carbonates under high-pressure conditions are limited.

In fact, most of the high-pressure studies on carbonates have been carried out in systems such as $CaCO_3$–$MgCO_3$–$FeCO_3$, due to their direct relevance in the mineralogy of the Earth's mantle, i.e. for studying the melting behavior of natural carbonated eclogite (Yaxley & Brey 2004; Dasgupta et al., 2004). Studies demonstrated that the composition of carbonates is highly dependent on pressure and bulk composition (Dasgupta et al. 2005). Experimental and theoretical works have grown significantly in recent decades to understand the carbon cycle in the depth of Earth. Carbon is stored within the mantle in various forms: the stability of carbonates in different environments is hence an important key issue in understanding the transfer of crustal carbon into the Earth or its recycling i.e. through volcanism or fluids carrying CO_2 (Dasgupta & Hirschmann 2006; Berner 2004; Dasgupta & Hirschmann 2010).

These studies revealed important crystallochemical changes at lower mantle pressures, like the modification in coordination number from [3] to [4] (Isshiki et al., 2004; Ono et al., 2005; Oganov et al., 2008; Arapan et al., 2007). Specifically, carbon transforms from a trigonal arrangement to tetrahedral carbonate units, which can polymerize presenting similarities with silicates (Merlini et al., 2015; Cerantola et al., 2017; Merlini et al., 2017). Calcite, $CaCO_3$ and dolomite $CaMg(CO_3)_2$ (Hazen, Downs, et al., 2013) constitute a significant fraction of crustal carbonates. They undergo several polymorphic phase transitions at high pressure (e.g. polymorphs $CaCO_3$-II, $CaCO_3$-III and $CaCO_3$-VI) up to adopting structures based on rings of three tetrahedra [C3O9] at pressures around 100 GPa (Merlini et al., 2020), as demonstrated by studies using single crystal synchrotron X-ray

diffraction. Experimental studies on carbonates with different compositions are limited. However, recent works on more complex systems, such as alkali and alkaline-earth metal carbonates, have highlighted an interesting complexity at much lower pressures, which can be related to petrologic carbonatitic processes: the experimental determination of the Na_2CO_3–K_2CO_3–$CaCO_3$–$MgCO_3$ system at HP-HT has shown that new classes of Ca-rich alkaline-earth carbonates stabilize at 6 GPa, such as the $Na_2Ca_3(CO_3)_4$ phase (Shatzky et al., 2016a, b; Podbornikov et al., 2019). These studies also reveal that these carbonates are primary phases in equilibrium on the liquid, and therefore could play a significant role in the fractionation of deep carbonatites. In addition to $Na_2Ca_3(CO_3)_4$, the stability of a burbankite-like structure was also observed at pressures higher than 4 GPa, for the composition $Na_2Ca_4(CO_3)_5$. This phase has also stimulated the exam of the possible stability of burbankite sensu strictu at high pressures, i.e. the possibility that REE elements can be stabilized in carbonates even at high pressures. Therefore, my dissertation also aims to attain the synthesis of La-burbankite with composition $Na_3Ca_2La(CO_3)_5$, in order to verify its stability at high pressure and temperature conditions compatible with carbonatite systems. High pressure and temperature crystallographic studies with diamond anvil cells and synchrotron X-ray diffraction will also allow to determine the elastic properties and density of this phase to verify the possible fractionation at Earth's upper mantle conditions.

I) The REE–CaO–SiO$_2$–H$_2$O–CO$_2$ system: the role of La and Y in the melting behavior and molecular structure

The origin of carbonatites has been much debated since Brogger's paper in 1921. Most of the known literature focused on a series of experimental studies in different experimental models in order to determine the origin of carbonatites related to alkaline rocks (for immiscibility relations) at crustal condition.

This experimental Ph.D. thesis is focused on REE bearing system that is closely related to carbonatites but few documented at mantle P-T conditions.

1.1 State of art

Wyllie, Tuttle and Boettcher investigated in the 60's numerous experimental systems with different purposes i.e. to study the role of alkali-carbonates and to have a direct bearing on the origin of calcite-apatite carbonatites.

Experimentally, phase equilibrium relationships in different systems i.e. the CaO–CO_2–H_2O and MgO–CO_2–H_2O systems have been studied over a wide range of pressure, temperature conditions and for varying water content to evaluate their effect on melting reactions (Boettcher et al., 1980; Irving & Wyllie 1975; Walter et al., 1962; Wyllie & Boettcher 1969; Wyllie & Tuttle 1959, 1960).

A CaO–CO_2 system has been studied at low pressure to investigate the reactions at various pressure with excess of CO_2. Pure calcite melts at 1339°C (Smith & Adams 1923; Wyllie & Tuttle 1959).

In CaO–CO_2–H_2O systems, it was experimentally demonstrated that at 1000 bars calcite precipitates from low temperature melts, liquid was not quenched in this system, and most of this is subsolidus (Figure 2a).

Figure 2 - Isobaric equilibrium diagram for the system CaCO₃-H₂O at 0.1 GPa. CC=calcite, V=vapor, L= liquid from Wyllie & Tuttle 1960. B) CaO-SiO₂-CO₂-H₂O system at 0.1 GPa pressure. Schematic diagram from Wylie & Haas 1965, the shaded area ABCD is the quaternary vapor-saturated liquidus surface connecting the ternary vapor-saturated liquidus field boundaries. The small, shaded area represents the vaporous surface giving compositions of vapors in equilibrium with liquids on the surface, ABCD and with a crystalline phase.

Eutectic melting occurs at temperatures down to 524 °C at 4 GPa from $CaCO_3$ + Ca $(OH)_2$ + vapor phase rich in CO_2 (Wyllie &Tuttle 1959; Wyllie & Boettcher 1969).

Hydrous melting of calcite-lime and magnesite-periclase assemblages starts at lower temperatures (< 900 °C) than pure carbonate (> 1200 °C) at upper mantle pressure conditions (Walter et al., 1962; Wyllie & Tuttle 1960).

In 1965, P.J Willye investigated the solid-liquid-vapor phases relationships in CaO–SiO_2–CO_2–H_2O system at temperatures below 950°C at 0.1 GPa pressure. From low-temperature liquids, it is therefore possible to precipitate hydrated and carbonated phases. A model system with addiction of silicate minerals was investigated to explain the relations between carbonatites and the associated alkaline rocks.

Boetcher in 1969 reported phase relations in the model system CaO–SiO_2–H_2O–CO_2 in the range of temperature 460-800°C and 0.4–4 GPa. Wyllie & Hass (1965) previously studied this system at 0.1 GPa. In this experimental study solid-liquid-vapor phase relations were described at temperature below 950°C to facilitate the precipitation of hydrated and carbonated phases. The phases obtained were: portlandite (CH), $Ca(OH)_2$; calcite (CC), $CaCO_3$; calciochondrodite (Ch), $Ca_5(SiO_4)_2(OH)_2$; spurrite (Sp), $Ca_5(SiO_4)_2CO_3$: dicalcium silicate (C_2S), Ca_2SiO_4; liquid (L) and vapor (V). Vapor phase was very H_2O rich.

Schematic isobaric equilibrium diagram for the whole system is represented in Figure 2b that shows the position of ternary liquids E (eutectics) and P (peritectic) under isobaric conditions taking part in reactions:

(1) CC + CH + V (V_1) + L(E_1) at 645°C.

(2) CH + Ch + V + L(E_2)   at 774 ± 10°C.

(3) Ch + V + C$_2$S + L(P$_3$)   at 955 ± 10°C.

(4) CC + Sp + L(P$_4$) + V (CO$_2$) at about 1180°C.

(5) Sp + V (CO$_2$) + C$_2$S + L(P$_5$) at about 1380°C.

Portlandite and calciochondrodite were the only hydrous phases recognized, no wollastonite or quartz were identified in this study. The SiO$_2$ content of the eutectic liquid E$_1$ is about 1%, when more SiO$_2$ is added to the system the liquidus temperature raises. These results suggest that Ca-rich magmas exists only with low dissolved silicate components.

Melting relationships in this system were extended by Boettcher & Wyllie in 1969 to 4 GPa; phases encountered experimentally appears coexisting with vapor-saturated liquidus and fluids at high pressure. In particular, phases present in this system have been: silica phases (S); (CC); aragonite (Ar), (Sp), (CH); (Ch); (C$_2$S). At pressure > 10kbars, wollastonite (W) and dellaite - hydrous phase (Y) appear on vapor saturated liquidus. Liquid mostly quenched to bubble-rich gasses in experiments at high temperatures. In ternary system CaO-CO$_2$-H$_2$O, the minimum melting temperature ranges from 645°C at 0.1 GPa to 525°C at 4 GPa.

Boettcher & Wyllie showed their results of phase relationships in a ternary hypothetical system MO–SiO$_2$–H$_2$O that include H$_2$O as volatile component (almost identical to CaO–SiO$_2$–H$_2$O with M hypothetical divalent cation). This ternary diagram is applicable at any ternary system with critical end points. In Figure 3, MO–H$_2$O has been assumed to be identical to CaO–H$_2$O with no critical end point up to 4 GPa, no hydrous phases were represented. Here, it is show only results at 0.97 and 1.5 GPa.

Figure 3 - Isobaric, polythermal diagram in the hypothetical ternary system MO-SiO$_2$-H$_2$O, modified from Boettcher & Wyllie (1969).

Figure 3a and Figure 3b show a miscibility gap that separate the vapor saturated liquids fields boundaries from the coexisting liquid-saturated vaporous one.

These boundaries are connected at the miscibility gap by isothermal dashed lines (L+V).

At increasing pressure, the solubility of solids in vapor phase increases, moving progressively further from the joint compounds H$_2$O and dotted lines are less coincident

with the compositions joint MS-H_2O and M_2S–H_2O. When pressure increases from 0.97 to 1.5 GPa, the miscibility gap becomes narrow, with no phases boundaries between L(S) and V(S) and liquid phases, as shown in Figure 2b, is able to continuously transform to vapor phase. Additionally, MO component dissolves to 0.97 to 1.5 GPa in the critical fluid extended to critical end point K_2. Figure 2b shows that ternary liquidus L(S) is connected with the ternary vaporous surface V(S) around the end of miscibility gap; critical end point K moreover become coincident with the points L (S, V, MS) and V (S, MS, L) and therefore dashed line L+V (S, MS) become short so L (S, MS) and V (S, MS) touch miscibility gap at K_2 point.

Figure 4 - Isobaric polythermal tetrahedra for the system CaO-SiO₂-CO₂-H₂O. Dark shaded surface is the vapor-saturated liquidus and the light shaded surface is the liquidus saturated vapors, modified from Boettcher & Wyllie (1969).

In Figure 4a and Figure 4b, the modifications necessary in the surface to obtain the critical equality of the liquid and the vapor in reaction is schematically exposed. This requires that second critical end point liquid and vapor became identically in compositions and properties. Figure 4 is similar to Figure 3: MO–SiO_2–H_2O has been taken as model for the system CaO–SiO_2–H_2O. At increasing pressure (Figure 3b), the miscibility gap in CaO–SiO_2–H_2O is reduced towards CaO–H_2O. This study reveals that melting temperature on this arrangement ranges from 637°C at 0.1 GPa to 515°C at 3.2 GPa, lower than CaO–CO_2–H_2O system. Results show also that silicate components remain soluble in low temperature synthetic carbonatites magmas with compositions near the join $CaCO_3$–$Ca(OH)_2$ and pressure up to 3 GPa. It also confirms that residual carbonatites magmas could be produced by fractional crystallization from silica-undersaturated magmas (SiO_2/CaO < 1/2 ratio), if a pressure of 0.97 GPa persists.

However, carbonatite melts are not so easily to study because they are typically non-quenchable (Genge et al., 1995) due to their properties; therefore, they need to be investigated at temperatures above the liquidus.

Two carbonate melt systems are known to quench as glasses at 0.1 GPa under laboratory conditions:

(1) $La(OH)_3$–$Ca(OH)_2$–$CaCO_3$–CaF_2–$BaSO_4$ (Jones & Wyllie, 1983);

(2) $MgCO_3$–K_2CO_3 (Faile et al., 1963; Ragone et al., 1966)

$La(OH)_3$–$Ca(OH)_2$–$CaCO_3$–CaF_2–$BaSO_4$ (Jones & Wyllie 1983) is the only system known to be quenched with REE. This experimental study investigated phase relations in a complex system near that of Sulphide Queen- Mountain Pass-California, where bastnaesite is very abundant (5-15% of the orebody), with addiction of other components to delineate the condition of fluorocarbonates and REE carbonates. Subsolidus assemblage consists of calcite, barite, portlandite, fluorite and lanthanum hydroxide. Phase relationships (Figure 5) indicate that for La_2OH values < 10% the liquidus conditions are between 650 and 800° C.

Figure 5 - Phase relations in La(OH)₃-Ca(OH)₂-CaCO₃-CaF₂-BaSO₄. Glass forming system showing region of melt which quench to glass (shaded areas). Abbreviations: CC-calcite, BA-barites, CF-fluorite, LH - Lanthanum hydroxide, L - liquid. After Jones and Wyllie (1986).

Glasses obtained are supercooled liquids; these represent quenched liquids with different volatile species.

Based on probe analysis liquid contains 33 wt.% of dissolved volatiles (about 13.7 wt.% of CO_2, 9 wt.% of H_2O, 6 wt.% of F, 3wt.% of SO_3).

This REE carbonate system have low eutectic temperature and low melt viscosities (Dobson et al., 1996). Results suggest that addiction of H_2O is essential to form liquid magma at low pressure and temperature near 650°C.

Due to the "anomalous'' formation of these carbonate glasses (from ionic liquids), the structures of these melts have been studied by infrared and Raman spectroscopy by Genge et al. (1995).

Figure 6 - Raman spectra of the carbonate internal mode region of (a) Mg-CO-K₂CO₃ and (b) La(OH)₃-Ca(OH)₂-CaCO₃-CaF₂-BaSO₄ glasses by Genge et., al 1995. Spectra are not baseline corrected. b) Raman spectra of La(OH),-Ca(OH)₂-CaCO₃-CaF₂-BaSO₄ glass. Note the infrared O-H stretching mode has been superimposed to highlight differences in activity.

Infrared absorption spectroscopy on La-bearing carbonate glass, in the system $CaCO_3$–$BaSO_4$–CaF_2–$Ca(OH)_2$–$La(OH)_3$, indicates the existence of CO_3 and CO_2 ion, and structurally bound CO (Figure 6). The Raman activity of the carbonate internal modes is similar to that of infrared activity.

The spectral activity of the O–H stretching region suggests that water exists both as molecular H_2O and OH. The activity of carbonate ion modes indicates the existence in the glasses of two populations of carbonate ion (molecular and dissolved as carbonate ion). This may correspond to a flexible pseudo-network structure, where, Ca and Mg (alkaline earth elements) act as bridging cations connected to carbonate groups by ionic bonds (i.e. crystalline carbonates), while other components, such as K, act as network modifiers (Genge et al., 1995b).

Comparison with IR spectra for silicate melts (Fine & Stolper 1986) suggests very low concentrations of CO_2 in carbonate melts. Infrared spectra of both carbonate glasses indicate the absence of a molecular CO_2 *v*3 stretching mode. The carbonate dissociation reactions that produce CO_2 and CO are one of the major controls on carbonate melt structure; CO_2 acts as a polymerizing agent, increasing melt viscosity (Eggler, 1978; Mysen & Virgo, 1980a). CO_2 in fact appears highly concentrated in low silica melts such as melilitite or kimberlite (Brooker et al., 2001; Massuyeau et al., 2015; Moussallam et al., 2015, 2016).

1.2 Experimental and analytical techniques

Starting materials were prepared as powder mixtures of a source of REE (La or Y) as $La_2(CO_3)_3$, La_2O_3 or Y_2O_3, amorphous SiO_2 and $CaCO_3$. These powder mixes were grinded in an agate mortar together with ethanol for at least 30 minutes to ensure a homogeneous compound.

In order to be able to recognize the signal of Ca in NMR analysis some starting materials have been prepared using constant isotopic ratio for $CaCO_3$. $CaCO_3$ was used for better recognize Ca and CO_2 signal in NMR analysis. Furthermore, our systems are Calcium Carbonatite rich and the local environment for Ca^{2+} is well constrained (Cormier & Cuello, 2013).

Sigma-Aldrich Calcium carbonate ($Ca^{13}CO_3$) enriched in ^{13}C (99 atom% ^{13}C) was used for NMR analysis. In this case, starting materials were grinded with ultrapure water.

Several compositions have been prepared in order to cover as wide as possible compositional space at variable SiO_2:$CaCO_3$ ratio, at fixed La_2O_3/Y_2O_3 value. This approach is required to investigate the highest calcite bearing system studied that could produce, homogeneous glasses after quenching. In fact, it is widely known that SiO_2 is quenchable and its melt produces homogenous glass, meanwhile $CaCO_3$ melt is unquenchable. Investigating all these bulk compositions, allow at identifying the maximum content of $CaCO_3$ in the melt that consents the formation of a glass and investigating structure and degree of glass polymerization.

Ten bulk compositions at fixed La_2O_3 or $La_2(CO_3)_3$ = 10 wt.% with SiO_2:$CaCO_3$ = 0.12; 0.2; 0.26; 0.28; 0.38; 0.5; 0.7; 0.8; 1 and 1.4 have been considered. Figure 7 shows the starting bulks as colored squares. Ten bulk compositions have been experimentally investigated in order to find the conditions for which the system melts and forms the liquid.

Figure 7 -Bulk compositions with different SiO_2:$CaCO_3$ ratio.

The double-colored squares in Figure 7 represent the bulk compositions that have been also analyzed using the NMR technique. In addition, bulk with SiO_2:$CaCO_3$ ratio 0.5 and 1.4 were preliminarily analyzed by NMR technique.

We also prepared seven bulk compositions with another REE, Yttrium, following the same experimental procedures; fixed Y_2O_3=10 wt.% with SiO_2:$CaCO_3$= 0.12; 0.28; 0.38; 0.5; 0.7; 0.8 and 1 (Figure 8).

For the experiments, La and Y, representing heavy and light Rare Earth Elements, were considered in two model hydrate systems to unravel their structural incorporation in melts at different SiO_2:$CaCO_3$ ratio.

Figure 8 - Y Bulk compositions with different SiO_2:$CaCO_3$ ratio.

For Nuclear Magnetic Resonance analytical procedure, calcite, the main source of CO_2 of experiments was added as 50% $Ca^{13}CO_3$ to investigate the CO_2 behavior and speciation in glasses.

Different capsules of Au, Pt and AuPt (Au_{60}–Pt_{40}) of 2.3-3- 5.6 mm of diameter were loaded with starting mixtures, added with approximately 5-10 wt.% of H_2O with micro syringe, and sealed while freezing the capsule to avoid the loss of volatile components.

Experiments at 1 GPa and 700–1250°C have been performed using single stage and both static and rocking end-loaded piston cylinders at the Laboratory of Experimental Petrology of the University of Milan (Italy).

Compared to the single stage system, the end loaded piston cylinder has an additional load, called end loaded, which allows at reaching higher pressures. Operation of the end-loaded piston cylinder is performed using a dual system of hydraulic jacks. The first, reaches a capacity of 150 tons and supplies the load to the assembly; the latter, double-acting, reaches a capacity of 1000 tons and provides the load containment of the bomb.

The single stage piston cylinder used for these experiments has 100-ton press.

The assembly is 42 and 34mm length for single stage and end-loaded piston cylinder apparatus, respectively. Asembly is included in the bomb, which contains a tungsten carbide core supported by concentric rims of steel.

For both piston cylinder apparatus experiments, we used NaCl (prepared by means of 20-ton press), Pyrex (with T> 900°C), graphite, and MgO assembly configuration.

Pressure is controlled by an automated hydraulic system and temperature is generated by a cylindrical furnace, monitoring with thermocouple, and regulated by a controller Eurotherm.

Starting materials were loaded in gold capsules (3 mm of diameter) for experiments at T < 900°C, and 2.3-5.6 mm of diameter Gold-Palladium (Au60Pd40) capsules for experiments at T > 900°C.

Capsules were loaded with 15-120 mg of starting material, with the amount of material based on the type of analysis. Capsules containing 120 mg of starting material were used for NMR analysis because these tests required major amount to be performed. A H_2O amount of about 5–10 wt.% has been added inside the capsules with micro syringe and sealed while freezing the capsule to avoid the loss of volatile components.

In order to verify that the outer capsule was perfectly sealed we inserted it in an oven at 110 ° C for 30 '', 45 '' and 60 '', and then weighed at each step: if there was no weight loss, the H_2O did not evaporated outside, and therefore the sealing was carried out correctly. A further verification was assessed with acetone or ultrapure water test placing the capsule under vacuum.

Experiments were carried out mostly in a single stage piston-cylinder apparatus as mentioned above, at pressure of 1 GPa and temperature from 700 to 1250 °C. We used MgO rods drilled to accommodate the capsule and MgO rods drilled to accommodate the thermocouple. Between two rods drilled MgO a corundum disk was placed at the top of the capsule to preserve it and to avoid the contact with thermocouple.

Experiments with same T were prepared with 3 capsules in one assembly drilled as showed in Figure 9.

Figure 9 - a) Drilled MgO; b) example of assembly of my experiments with temperature > 900°C.

The furnace was a graphite heater surrounded by Pyrex glass and NaCl sleeve. NaCl sleeve was used for experiments with T < 900°C.

At the top of the entire assembly, a pyrophyllite plug was used to ensure the electrical contact.

Pyrex glass were first heated to T= 400 °C with temperature rate of 50 °C/minute, then pressurized to the final pressure value of 1 GPa and finally heated to the required experimental temperature with an increase rate of 100 °C/minute.

Temperature was measured with K-type (Ni-Cr / Ni-Al) and S-type thermocouple (Pt-Pt90Rh10).

We used K-Type thermocouple for experiments with T < 900°C and S-type thermocouple for experiments with T > 1100°C.

These experiments were performed for a variable run time ranging between from 4 hours (for experiments at high temperature) to 3 days (for experiments at low temperature, about 700-800°C). Mostly of experiments at 1200-1250°C were performed for 24h and then quenched.

After experimental runs capsules were extract from assemblies, they were cleaned, embedded in expoxy resin, and dried in the oven at 75°C for 2 hours, then polished and lowered by hand by means of sandpaper (320, 600, 1200 μm size) and diamond paste (9-1 μm size) to avoid any contact with water to better characterized by BSE images, X-ray diffractometry, Raman spectroscopy and chemically analyzed by electron microprobe.

After polishing, samples were further cleaned with ultrasound machine by inserting the mount into a beaker containing hexane. No water was used to avoid the possible dissolution of the carbonates.

Some capsules, in particular those used for NMR analysis, were dissolved by HCl+H_2O (1:1 ratio) mixture at 80 °C for 1-2 hours. For NMR analysis, after runs the capsules were opened with nippers and then material was extracted.

As described above, run products were carefully prepared to avoid any contact with water and polished with diamond paste and have been characterized by BSE images, X-ray diffractometry, Raman spectroscopy, Nuclear Magnetic Resonance spectroscopy and chemically analyzed by electron micro probe analyzer (EMPA).

The EMPA analysis were performed at the Department of Earth Sciences "Ardito Desio'', University of Milan. The electron microprobe instrument installed at our department is a Jeol JXA – 8200 Superprobe equipped with five WDS-wavelength-dispersive spectrometers, EDS and cathodoluminescence detector. The Electron Microprobe Analyzer (EMPA) allows us to characterize chemically the run products and to obtain information of texturally features.

In order to characterize the mineral and glass compositions in experiments, we worked at 15 kV, 5 nA, using beam size of 1microns for minerals and 5 microns for glasses.

Some samples were analyzed also by single-crystal X-ray diffraction at the Department of Earth Sciences "Ardito Desio'' using a Rigaku XtaLAB Synergy-S diffractometer, equipped with a HyPix-6000HE HPC area detector and with a PhotonJet-S Mo-Kα (λ = 0.71073 Å) micro source operating at 50 kV and 1 mA.

All samples were analyzed by Micro-Raman spectroscopy (Figure 10) that is able to acquire spatially resolved Raman spectra by combining the conventional Raman

spectrometer with an optical microscope. This non-destructive and non-invasive technique has a high spatial resolution (1 µm or less) and allows for measurements in very small areas (micrometer range), so fewer amount of samples are required and certain effects may also be enhanced over very localized regions.

Raman spectra were collected using and Horiba LabRAM HR Evolution microscope with a Syncerity OE detector, using Nd-Yag 532 nm/100mW laser sources with Ultra Low Frequency (ULF) filters at the Department of Earth Sciences, University of Milan.

The system was calibrated using the 520 cm^{-1} Raman line of metallic silicon. Reflected light optic were used on a polished mounts and the analysis were performed using a 100x objective and 600 r/mm grating.

Spectra were collected using laser power to 25% to 100%, an exposure time of 20-30 s and 2-3 accumulations to eliminate possible spike; the spectra were also processed using LabSpec v.6 (Horiba ®). Peak positions were obtained by fitting Gaussian peaks on Origin Pro programme.

Figure 10 - MicroRaman Horiba LabRAM HR Evolution.

In this study, we investigated at the molecular scale the relationship between selected REE, Lanthanum and Yttrium respectively, and CO_2 thanks a collaboration with Morizet Yann LPG (Nantes).

NMR spectroscopy is applied to the oxide glass structure description at a strong level of details thanks to the development of methods exploring heteronuclear and homonuclear correlations. These structural data are essential to characterize glass properties like chemical durability, thermal stability, or behavior to irradiation.

Nuclear Magnetic Resonance is a highly efficient technique to analyze molecules at the atomic scale, thanks to magnetic properties of some of their nuclei (mainly ^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{17}O) – hence the name "nuclear".

These analyses were performed at IMN Jean Rouxel (Nantes). Solid State La NMR was performed with a Bruker Avance III 500 MHz spectrometer. The ^{139}La MAS NMR spectra were acquired with a 2.5 mm CP/MAS probe and a MAS frequency of 30 kHz. The bulk compositions were prepared with multiple isotopic enrichment for conducting a thorough NMR investigation including ^{29}Si and ^{17}O NMR spectroscopy. As a result, two types of compositions were prepared: ^{89}Y-bearing and ^{139}La-bearing doped with 1) Ca^{13}CO$_3$ as the source of Ca and CO$_2$, 2) ^{29}SiO$_2$ and Si^{17}O$_2$ for further investigation on the network connectivity and anionic environment. The aim of this technique in this study is to assess the fundamental relationship between ^{139}La or ^{89}Y and ^{13}C through NMR spectroscopy considering that NMR is highly dependent on the element concentration.

A total of thirty-seven experiments were carried out in the two systems CaO–SiO$_2$–La$_2$O$_3$–H$_2$O–CO$_2$ and CaO–SiO$_2$–Y$_2$O$_3$–H$_2$O–CO$_2$ to allow me to define phase relationships, essential for the carbonatites magmatism.

Experiments were carried out at different durations variable to few hours to 3 days, in some cases with difficulty in identifying the textures.

Despite the experiments performed at different temperature and compositions, as I will show below, the phases assemblages obtained are very similar to each other.

Ten different compositions were investigated to better characterize the system.

In this chapter will be presented microscopy observations by EMPA analysis and descriptions of textural and mineral assemblage for the synthesis of Na$_3$Ca$_2$La (CO$_3$)$_5$ at 5 GPa and experiments in CaO–SiO$_2$–La$_2$O$_3$–H$_2$O–CO$_2$ and CaO–SiO$_2$–Y$_2$O$_3$–H$_2$O–CO$_2$ systems at 1GPa at different SiO$_2$:CaCO$_3$ ratio. Phase assemblages will be characterized by XRD and microRaman spectroscopy.

Experimental results in the system CSLCH and CSYCH are presented in Table 1 and 3 together with run conditions.

In Tables are reported: name of the experiment (RUN#), capsule material used, SiO$_2$:CaCO$_3$ ratio (from highest to lowest), temperature (T) from lowest to highest for each bulk analyzed, pressure (P), assembly (full salt for experiments < 1000°C of temperature and salt+pyrex for experiments > 1000°C of temperature), thermocouple used (TC), apparatus, run time in hours and run products. Table 1 (CaO–SiO$_2$–La$_2$O$_3$–H$_2$O–CO$_2$ system) is divided into three blocks:

-   subsolidus experiments in which each set of bulk has been investigated at the same pressure and different temperatures (700–1110°C);
-   near liquidus experiments;
-   supraliquidus experiments.

For investigated systems, the solidus is located between 1000 and 1200°C, depending on bulk composition. The subsolidus and near solidus experiments lasted up to 168 hours while supraliquidus experiments lasted 24 hours.

Below, it is firstly presented the run products of the subsolidus, then the near solidus/supra-liquidus results.

SYSTEM: CaO-SiO$_2$-La$_2$O$_3$-H$_2$O-CO$_2$									
SUBSOLIDUS									
RUN#	Capsule	SiO$_2$/CaCO$_3$	T	P	Assembly	TC	Apparatus	Run time (hrs)	Run product
DS4	Au 3mm	1.4	700	1GPa	Full salt	K	Single stage	167	Qz,CC, Ca-La silicate
DS9.3	Au 2.3mm	1.4	1000	1GPa	Full salt	K	Single stage	165	CC, wo, Ca-La silicate
DS3	Au 3mm	1	700	1GPa	Full salt	K	End-loaded	160	Qz,CC, Ca-La silicate
DS7	Au 3mm	1	700	1GPa	Full salt	K	Rocking	94	Qz, CC, Ca-La silicate
DS9.2	Au 2.3mm	1	1000	1GPa	Full salt	K	Single stage	165	Qz, CC, Ca-La silicate
DS2	Au 3mm	0.7	700	1GPa	Full salt	K	End-loaded	168	Qz,CC, Ca-La silicate
DS5	Au 3mm	0.7	800	1GPa	Full salt	K	Single stage	5	Qz,CC, Ca-La silicate
DS9.1	Au 2.3mm	0.7	1000	1GPa	Full salt	K	Single stage	165	CC, Wo, Ca-La silicate
DS13	Pt 2.3mm	0.5	700	1GPa	Full salt	K	Rocking	45	Ca-La silicate,CC
DS11	Pt 3mm	0.5	800	1GPa	Full salt	K	Rocking	117	Ca-La silicate, CC
DS12	Pt 3mm	0.5	900	1GPa	Full salt	K	Rocking	45	Ca-La silicate,CC
DS16	AuPd 2.3	0.5	1100	1GPa	Salt+pyrex	K	Rocking	90	CC-Wo, Ca-La silicate
DS20	AuPd 2.3	0.12	700	1GPa	Full salt	K	End-loaded	72	Qz, CC. Ca-La silicate
LOW MELT FRACTION RUN CONDITIONS									
RUN#	Capsule	SiO$_2$/CaCO$_3$	T	P	Assembly	TC	Apparatus	Run time (hrs)	Run product
DS9.3	Au 2.3mm	1.4	1000	1GPa	Full salt	K	Single stage	165	CC, Wo, Ca-La silicate
DS9.2	Au 2.3mm	1	1000	1GPa	Full salt	K	Single stage	165	Qz, Wo, Ca-La silicate
DS9.1	Au 2.3mm	0.7	1000	1GPa	Full salt	K	Single stage	165	Qz, CC, Wo, Ca-La silicate
DS15	AuPd 2.3	0.7	1200	1GPa	Talc+pyrex	S	Rocking	17	Wo, Ca-La silicate
DS16	AuPd 2.3	0.5	1100	1GPa	Salt+pyrex	K	Rocking	90	CC-Wo, Ca-La silicate
HIGHT MELT FRACTION AND SUPRA LIQUIDUS RUN PRODUCTS									
RUN#	Capsule	SiO$_2$/CaCO$_3$	T	P	Assembly	TC	Apparatus	Run time (hrs)	Run product
DS10	Pt 2.3mm	1.4	1250	1GPa	Salt+pyrex	S	Single stage	24	glass
DS24	AuPd 2.3	1	1250	1GPa	Salt+pyrex	S	Single stage	24	glass
DS25	AuPd 2.3	0.7	1250	1GPa	Salt+pyrex	S	Single stage	24	glass
NMR50La	AuPd 5.6	0.8	1250	1GPa	Salt+pyrex	S	Single stage	24	glass
NMR60La	AuPd 5.6	0.5	1150	1GPa	Salt+pyrex	K	Single stage	24	glass
DS23	AuPd 2.3	0.38	1250	1GPa	Salt+pyrex	S	Single stage	24	glass

Table 1 - Run Table for CaO-SiO$_2$-La$_2$O$_3$-H$_2$O-CO$_2$ system. Abbreviations: TC=thermocouple, Au=gold, Pt=platinum, AuPd=gold-palladium; qz=quartz, cc=calcite, wo=wollastonite.

At 1 GPa and 700-800-900-1100°C, all experiments reported in Table 1, for different bulk compositions at different SiO$_2$:CaCO$_3$ (from 0.12 to 1.4) ratio, contain calcite and quartz coexisting with a Ca-La-silicate.

Subsolidus assemblage for CaO–SiO$_2$–La$_2$O$_3$–H$_2$O–CO$_2$ system consists of calcite, quartz, and Ca-La-silicates.

Figure 11 - a) BSE images of SiO₂:CaCO₃= 0.7 at 700°C that show quartz (qz), calcite (cc) and Ca-La-silicate; b) SiO₂:CaCO₃= 1.4 show anhedral and subhedral qz, cc and Ca-La-silicate grains; c) SiO₂:CaCO₃= 0.7 at 800°CBSE subhedral crystals of qz and cc and Ca-La-silicates; d) SiO₂:CaCO₃= 1 microcrystalline aggregates of Ca-La-silicate.

Selected BSE images (Figure 11) show that at 700-800-900°C investigated bulks with SiO_2:$CaCO_3$ ratio of 0.7 and 1 presents subhedral and anhedral crystals of calcite and quartz of ~10-15 µm of size and Ca-La-silicate crystals (Ca-La silicate), this latter occuring mostly as microcrystalline aggregates ~5-8 μm. In place, they occur also as distinctive elongate prism with a pseudo-hexagonal prismatic shape.

About 10-20 points of Ca-La-silicates crystals were measured for each experiment by EMPA and their compositions are shown in Table 2. Analyses show up to 62-66 wt.% of La_2O_3, 9-11 wt.% CaO and 22-24 wt.% SiO_2.

Major element compositions (wt.%) of syntetic crystals of calcium-lanthanum silicate in this study									
Ca-La-silicate	DS9.2-1 .1	DS9.2-4 .1	DS9.2-5 .1	DS9.2-6 .1	DS9.2-11 .:	DS9.2-9 .1	DS9.2-11 .:	DS9.2-9	DS9.2-2 .2	DS9.2-9 .2
SiO2	23.28	23.45	23.34	23.32	22.46	23.32	23.51	23.14	23.39	23.14
La2O3	64.23	63.76	65.39	64.59	62.73	64.13	63.97	64.08	63.73	64.08
CaO	11	11.02	11.16	11.38	11.48	10.96	11.22	11.44	11.94	11.44
Tot	98.51	98.23	99.89	99.29	96.67	98.41	98.7	98.66	99.06	98.66
apfu										
Si	3.22	3.24	3.20	3.21	3.18	3.23	3.24	3.20	3.21	3.20
La	3.28	3.25	3.31	3.27	3.27	3.28	3.25	3.27	3.22	3.27
Ca	1.63	1.63	1.64	1.68	1.74	1.63	1.65	1.70	1.75	1.70

Table 2 - Major element compositions of Ca-La- silicate, chemical formula has been calculated on 13 oxygens.

At 1000°C, wollastonite forms and coexists with Ca-La-silicate and calcite or quartz depending on the starting bulk composition.

BSE images of experiments reported in Table 2 show subhedral wollastonite and calcite crystals and anhedral crystals of quartz.

Ca-La-silicate crystals are present in the form of micro-cristalline aggregates with a maximum size of 7μm (Figure 12a).

Presence of silica spherules less than 5 μm in size (Figure 12b) may testify the coexistence of a high-pressure fluid.

Figure 12 - a) BSE image of SiO$_2$:CaCO$_3$=0.7 show anhedral calcite, microcristalline Ca-La-silicates and subhedral wollastonite; b) SiO$_2$:CaCO$_3$=0.7 show silica spherules.

The bulk composition with the lowest SiO$_2$:CaCO$_3$ ratio (0.14; DS19 experiment), run at 1200°C, did not quench to glas; rather, it shows calcite with typical dendritic textures (Figure 13 a-b).

BSE images of experiment DS14 (Figure 13c) with SiO$_2$:CaCO$_3$= 0.5 show quenched products at the bottom of the capsule characterized by growth of feathery crystals, wollastonite and micro-crystals of Ca-La-silicate.

Figure 13d shows glass obtained from bulk composition with low SiO$_2$:CaCO$_3$= 0.2 characterized by presence of small (3 μm) Ca-La-silicates texturally subhedral.

Figure 13 - a-b) Dendritic textures and rounded calcite crystals in DS19; c) BSE image in DS14 with Ca-La-silicate in wollastonite and dendritic textures; d) DS21 glass with Ca-La-silicate.

Figure 14 a-b, shows a part of NMR 71.5-La experiment. This test was performed using 5.6 AuPd capsule, salt-Pyrex assembly and S-type thermocouple and the run time was approximately 24 hours at 1250°C. BSE images for this part of the experiment with $SiO_2:CaCO_3$ ratio= 0.26 show calcite, rounded wollastonite and Ca-La-silicate crystals.

The resulting reaction shows a simplectitic texture characterized by vermicular rods (< 40 µm) of wollastonite included in calcite crystals.

These microstructures are common in metamorphic rocks (Vernon 2004) such as mantle peridotites (e.g., Takahashi & Arai, 1989; Godard & Martin, 2000), crustal amphibolites (e.g. Misch & Onyeagocha, 1976), eclogites (e.g. Joanny et al., 1991), kimberlites (e.g. Ringwood & Lovering, 1970). Symplectites are considered an important indicator of pressure–temperature–time paths during metamorphism (Lanari et al., 2013).

The origin and formation of symplectite microstructures include: (1) crystallization from melt (e.g., Williams, 1932; Hibbard, 1979), (2) exsolution during cooling (e.g. Schwantke,

1909; Moseley, 1984) and (3) solid-state replacement reactions triggered by changes in P-T conditions (e.g. Becke, 1908; Cruciani et al., 2008).

In this case, we worked at isobaric and isothermal conditions and these textures may be formed because of interaction with crystals (wollastonite and calcite) and internal fluids (H_2O in our cases) by hydration reactions (i.e. hydrothermal experiments at low temperature - 600°C) or it may be interpreted as exolution during cooling.

The exolutions during cooling would seem to better explain the formation of these structures. In Figure 14 a-b, in fact, Calcium-Lanthanum silicate crystals and rounded wollastonite shapes remained unaltered, thus confirming this hypothesis.

Figure 14 - a-b) Simplectitic textures with rounded wollastonite crystals, calcite and Ca-La-silicates.

In $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system, at 1 GPa, partial melting in bulk compositions with $SiO_2:CaCO_3$ = 0.38; 0.5: 0.7; 0.8; 1 and 1.4 has been observed at 1250°C, 1150°C and 1200°C respectively, as reported in Table 1.

Run products completely quenched to a glass and show evidence of fluid present conditions (Figure 15 - Figure 16). Glasses observed were not so much transparent (Figure 16); in fact, bubbles are present (vapor phases).

There are menisci (Figure 15a) that indicate the presence of vapor coexisting with the liquid.

At the microprobe scale, have been observed on in the runs with initial $SiO_2:CaCO_3=1.4$, we observed in the glass some particles of less than 1µm in size (Figure 15b). The tiny size, however, does not allow their identification by microprobe and, as a result, their interpretation as vesicles, immiscible liquid or quenched products remained undetermined.

Generally, BSE images of glasses obtained by the complete melting of bulks with $SiO_2:CaCO_3$ = 0.38; 0.5; 0.7; 0.8; 1 and 1.4 show a homogeneous and porous glass (Figure 16 a-b).

Figure 15 - a) DS10 glass, at 1 GPa, 1250°C, apparently homogeneous glass with menisci; b) DS10 glass with micro particles.

Figure 16 - a) DS18 glass, 1GPa, 1250°C; b) NMR50La glass at 1 GPa, 1250°C. BSE image shows a porous glass.

Experimental results in the system $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ (CSYCH) are presented in Table 3 together with run conditions.

As for CSLCH system, in Table 3 are reported: name of the experiment (RUN#), capsule material used, $SiO_2:CaCO_3$ ratio (from highest to lowest), temperature (T), pressure (P), assembly, thermocouple used (TC), apparatus, run time in hours and run products.

Experiments in $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ were carried out at the same P-T conditions; experiments were performed in single stage piston cylinder apparatus at 1250°C with the same assembly (salt+pyrex) for all bulk investigated.

We investigated high temperatures (T =1250°C) in order to obtain glasses to study their structure and compare it with that of the $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ system.

In Table 3 are reported:
- near-liquidus experiments;
- supra-liquidus experiments.

The run time for all experiments of this system was of 12-24 hours at 1250°C.

SYSTEM: CaO-SiO$_2$-Y$_2$O$_3$-H$_2$O-CO$_2$									
RUN#	Capsule	SiO $_2$/CaCO $_3$	T	P	Assembly	TC	Apparatus	Run time (hrs)	Run product
DS30	AupD 2.3	1	1250	1 Gpa	salt+pyrec	S	Single stage	12	Ca,Y silicate
NMR50Y	AuPd 5.6	0.8	1250	1GPa	Salt+pyrex	S	Single stage	24	glass,wo
DS29	AupD 2.3	0.7	1250	1 Gpa	Salt+pyrex	S	Single stage	4	Glass, Ca-Y silicate
DS26	AupD 2.3	0.5	1250	1 Gpa	Salt+pyrex	S	Single stage	24	Glass, Ca-Y, silicate
DS31	AupD 2.3	0.38	1250	1 Gpa	salt+pyrec	S	Single stage	12	CC, Ca-Y silicate
NMR71.5L	AuPd 5.6	0.26	1250	1 Gpa	Salt+pyrex	S	Single stage	24	cc,wo, Ca-La silicate
DS27	AupD 2.3	0.28	1250	1 Gpa	Salt+pyrex	S	Single stage	24	Glass, Ca-Y, silicate
DS28	AupD 2.3	0.12	1250	1 Gpa	Salt+pyrex	S	Single stage	4	cc. Ca- Y, silicate, glass

Table 3 - Run Table for CaO-SiO$_2$-Y2O$_3$-H$_2$O-CO$_2$ system. Abbreviations: TC=thermocouple, AuPd=gold-palladium; cc=calcite, wo=wollastonite.

BSE images of DS27 with SiO$_2$:CaCO$_3$= 0.28 ratio (Figure 17a) show a porous glass on the top of the capsule full of micro-crystals of Ca-Yttrium-silicate.

On the bottom of capsule, large (< 300 μm length) sub-euhedral crystals Ca-Yttrium are observed (graphic texture).

For SiO$_2$:CaCO$_3$ ratio= 0.7 (Figure 17b), BSE images show a porous glass with Ca-Yttrium-silicate (Ca-Y-silicate) crystals and only on the bottom of capsule quenched products.

Figure 17 - a) DS27 experiment, 1 GPa at 1250°C, BSE image show on the top glass and microcristals of Ca-Y-Silicate and on the bottom macro crystals with prismatic shape; b) DS29 experiment, 1 GPa at 1250°C, show pure glass on the top and dendritic textures.

About 5-10 points of Ca-Y-silicates crystals were measured for each experiment by EMPA and the compositions of single points are shown in Table 4. Analyses show up to ~ 43–54 wt.% of Y$_2$O$_3$, 15–22 wt.% CaO and 27–29 wt.% SiO$_2$.

Major element compositions (wt.%) of syntetic crystal of calcium-yttrium-silicates in this study							
Ca-Y-silicate	DS27-4	DS27-5	DS27-6	DS28-4	DS28-7	DS28-10	DS28-11	DS28-12
SiO_2	28.49	28.21	28.16	27.45	27.63	28.15	27.63	27.86
CaO	16.07	16.19	16.07	16.98	16.96	16.02	15.92	15.82
Y_2O_3	53.03	53.45	53.31	52.4	53.24	53.91	53.99	53.69
Tot	97.59	97.85	97.54	96.83	97.83	98.08	97.54	97.37
apfu								
Si	3.18	3.15	3.15	3.11	3.10	3.14	3.11	3.14
Y	3.15	3.18	3.18	3.15	3.18	3.20	3.24	3.22
Ca	1.92	1.94	1.93	2.06	2.04	1.92	1.92	1.91

Table 4 - Major element compositions of Ca-Y-silicate; chemical formula has been calculated on the basis of 13 oxygens.

BSE images of experiments with $SiO_2:CaCO_3= 0.28–0.5$ ratio show a homogeneous and porous glass (Figure 18 a-b).

Figure 18 - a) A part of NMR50Y experiment, BSE image shows a porous glass; b) DS26 experiment shows glass with bubbles indicating the coexistence with a vapor phase.

In the $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ system, the bulk composition with the lowest $SiO_2:CaCO_3$ ratio (0.28), at 1200°C, does not quench to glass, but it shows calcite with typical dendritic textures (Figure 19 a-b).

Figure 19 - a) DS28 experiment shows prismatic Ca-Y-silicates and roundend calcite crystals; b) DS30 experiment shows calcite and microcrystals of Ca-Y-silicates.

1.3 Results: XRD, chemical composition, Raman and preliminary NMR results of calcium -Yttrium/Lanthanum silicates

Quantitative chemical analyses of Ca-La-silicates and Ca-Y-silicates were obtained by EMPA analysis in polished and carbon coated mounts at the Department of Earth Science of University of Milan. Major and minor elements were determined by EMPA analysis.

After identification of phases (peaks search) present in the experimental charges by X'Pert HighScore Plus program, we made the refinement using GSAS program (Figure 20) with relative CrystallographicInformationFile´s (CIF) files.

Figure 20 - X-Ray diffraction pattern refined by GSAS program. DS9.3 experiment, SiO_2:$CaCO_3$=1.4, 1000°C, 1 GPa.

The structure of synthetic single crystal of Calcium-Lanthanum and Calcium- Yttrium silicates were obtained by a single-crystal x-ray diffraction measurement at room temperature using a four circles κ-geometry Rigaku XtaLAB Synergy diffractometer.

Experiments (mounts) were attached on a metallic pin and mounted on a goniometer head. The wavelength used for the analyzes is that of molybdenum, 0.7093 Angstrom.

In Figure 20 and Figure 21 the X-ray diffraction patterns of the DS9.3 and DS5 experiments are shown; DS9.3 experiment was performed at 1000°C, 1GPa with SiO_2:$CaCO_3$ ratio 1.4; it presents two main peaks characteristic of wollastonite (120) and Calcium-Lanthanum silicate. Quantification by GSAS provided 86.5% wollastonite and 13.5% Ca-La-silicate (121). DS5 experiment was performed at 700°C, 1GPa with SiO_2:$CaCO_3$= 0.7, it showed calcite, quartz and Ca-La-silicate peaks.

Figure 21 - X-Ray diffraction pattern of DS5 on CaO-SiO_2-La_2O_3-H_2O-CO_2 system with SiO_2:$CaCO_3$=0.7. 800°C, 1GPa.

The single crystal X-ray diffraction pattern for Ca-Y-silicate reveals that its structure crystalizes in a hexagonal lattice.

The refined unit cell parameters are a = 9.4082(8), c = 6.7998(5) Å and V = 521.24(7) Å^3 at ambient conditions.

The structural solution and refinement using the crystallographic software CrysAlis indicates that the Ca-Y-silicate crystalizes in the hexagonal $P6_3/m$ space group (Figure 22) and shows an apatite-type structure with similarities with britholite natural compound. The refined atomic coordinates are reported in Table 5, considered each atomic site fully occupied and occupancies according to chemical analysis.

Structure parameters					
	x	y	z	Occ.	U
Y1	0.24839	0.25236	0.25	0.658	0.01
Ca1	0.24839	0.25236	0.25	0.342	0.01
Y2	0.66667	0.33333	-0.00195	0.545	0.014
Ca2	0.66667	0.33333	-0.00195	0.455	0.014
Si1	0.36866	0.39607	0.75	1	0.01
O1	0.53039	0.40492	0.25	1	0.019
O2	0.24883	0.33931	0.56202	1	0.029
O3	0	0	0.25	1	0.079
O4	0.48773	0.319	0.75	1	0.018

Table 5 - Atomic coordinates, site occupancies and equivalent displacement parameters (Å2) of Ca-Y- silicate.

The refinement and occupancies reported in Table.5 indicate a Y/Ca ratio 3 to 2 with chemical formula: $(Y_{3.01} Ca_{1.99})(Si_3 O_{12})(OH)$.

Figure 22 - Crystal representation with bonds and tetrahedra of Calcium-Yttrium silicates.

Chemical analyzes have a closure <100%, thus indicating the presence of the OH group.
The empirical formula calculated from the analyses and based on 13 oxygens a.p.f.u. is $Si_3Ca_{1.934}Y_{3.066}O_{12}(OH)$. Based on the empirical formula calculated on the EMPA data, there is the presence of some atomic substitution.
Figure 23 dislays the refined results that show the relationship between calculated structural factors (F.calc) and observed one (F.obs).

Figure 23 - F.obs Vs F.calc diagram for the refined structure by Jana2006 crystallographic program.

For Calcium-Lanthanum silicate crystals the absence of large crystal sizes (<10 µm) did not allow a structural analysis. However, on the basis of the ratio La-Ca to Y (higher than the La one; 3.50 to 1.50), we defined an intermediate formula between $La_{3.5}Ca_{1.5}(Si_3O_{12})O_{0.5}(OH)_{0.5}$ and $La_{3.2}Ca_{1.5}(Si_3O_{12})O_{0.2}(OH)_{0.8}$ with similarities with empirical formula between $La_3Ca_2(Si_3O_{12})OH$ and $La_4Ca(Si_3O_{12})O$.

Figure 24 - Structural structure of Lanthanum silicates.

Calcium-Yttrium (Figure 22) and Calcium-Lanthanum (Figure 24) silicates crystals have chemical similarities with the apatite $Ca_5(PO_4)_3$[F, OH, Cl] structure natural compound.

Ca-La-silicate phase and Ca-Y-silicates with an apatite-type structure and pseudo-hexagonal prismatic shape are chemically homogeneous in all the experiments (Figure 25 and Figure 26).

In Figure 25 and Figure 26, chemical compositions (from EMPA analysis) of Ca-La-silicate and Ca-Y-silicate phases are represented by rhombuses of different colors; each color represent a bulk composition with specific $SiO_2:CaCO_3$ ratio indicated in the legend.

Figure 25 - Mineral chemistry of Ca-La-silicates, 700-1150°C, 1 GPa for $SiO_2:CaCO_3$=0.12; 0.26; 0.7; 0.8; 1 and 1.4 ratio.

Figure 26 - Mineral chemistry of Ca-Y-silicates, 1250°C, 1 GPa for $SiO_2:CaCO_3$=0.12; 0.28; 0.38; 0.5; 0.7 and 1 ratio.

The glass compositions for both systems are reported in Figure 27 and Figure 28, as for silicate REE chemical compositions, squares represent starting bulk compositions and rhombuses each chemical analysis.

For $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system, we obtained homogeneous glasses for bulk compositions of $SiO_2:CaCO_3$ = 0.28; 0.38; 0.5; 0.7; 0.8; 1 and 1.4 ratio; glasses compositions are consistent with the starting mixtures (Figure 27).

Figure 27 - Glass compositions for CaO-SiO2-La2O3-H2O-CO2 system, 1150-1250°C, 1 GPa. Legend: *starting bulk compositions with Lanthanum carbonate; + starting bulk compositions doped on C^{13}.

Figure 28 - Glass compositions for CaO-SiO2-Y2O3-H2O-CO2 system, 1250°C, 1GPa.

Samples were analyzed by Raman in order to study the molecular structure of low-silica and carbon-rich melts, defined transitional and in particular to evaluate the effect of CO_2 on their structure.

Raman spectra were collected using Horiba LabRAM HR Evolution microscope with a Syncerity OE detector and argon ion laser at wavelength of 532 nm at the Department of Earth Sciences, University of Milan.

Crystals and glasses analyses were performed in confocal mode with hole (100 μm) and focused through the objective with the highest magnification (100×).

Spectra were collected in the 50–1200 cm^{-1} (silicate-carbonate network domain) and 2800–4000 cm^{-1} (OH + H_2O domain) shift ranges relative to the exciting laser light.

LabRAM HR Evolution is equipped with a grating with 600 and 1200 grooves/mm and a CCD detector. We used a grating of 600 grooves/mm to cover each domain in one scan choosing short counting times (2-3accumulations for 20 s).

Figure 29 - Raman spectra of quartz; a) wollastonite; b) and calcite; c) in subsolidus phase assemblages.

Spectral frequency position was calibrated with a standard source, silicon 520.7 cm^{-1}. Raman shift. The spectra obtained from experiments in subsolidus and near-liquidus conditions, are calcite, quartz, wollastonite (Figure 29) and Ca-La-silicate (for La system) or Ca-Y-silicate (for Y system).

In particular:

- Calcite shows an intense band at 1085 cm^{-1} arising from the symmetric stretching vibration of the carbonate group. There are also weak bands arising from other carbonate vibrations, the in-plane bending mode at 700 cm^{-1} and the strong band at 280 cm^{-1} is due to the lattice vibrations of the calcite crystal (Figure 29a).

- On quartz spectra are observed bands in the low-frequency portions of the spectrum, in particular the highest intensity mode occurs at 465 cm^{-1} (Figure 29b).
- Wollastonite is identified in experiments at about more than 1000 °C and shows intense typical peak at ∼967 cm^{-1} (Figure 29c).

Figure 30a and Figure 30b show Raman spectra acquired under green laser excitation for Calcium-Lanthanum silicate in the range 50–3800 cm^{-1} and Calcium-Yttrium silicate in the range 50–1200 cm^{-1} Raman shift.

Spectra are similar each other's (see 50-1200 cm^{-1} range) and characterized by a weak OH stretching modes at 3200–3250 cm^{-1} Raman shift, weak presence of CO_3^{2-} modes and C-H stretching region (3000–2800 cm^{-1}).

Figure 30 - Raman spectra of Ca-La-silicate and Ca-Y-silicate phases from DS9.2 and DS27 experiments.

Glass structures are closely related to the melt structures and the solubilities of elements that preferentially form when they are quenched.

Spectral glass ranges for CaO−SiO$_2$−La$_2$O$_3$−H$_2$O−CO$_2$ system studied at different SiO$_2$:CaCO$_3$ ratio are reported in Figure 31a (100−1200 cm^{-1}), Figure 31b (500−1200 cm^{-1}), Figure 31c (500−1200 cm^{-1}) and Figure 31d (500−1200 cm^{-1}).

Figure 31 – Raman spectra of glasses at different SiO₂:CaCO₃ ratio in the system CSLCH.

Raman spectra of glasses in CSLCH system exhibit two main characteristic regions: a low frequency region (LF: ~400 to ~600 cm^{-1}) and a high-frequency region (HF: ~800 to 1200 cm^{-1}).

Raman spectra for all glasses reported in Figure 31 show a strong peak (it depends on the bulk compositions) at 1078–1080 cm^{-1} related to CO_3^{2-} stretching vibrations.

For Ca-rich bulks (Figure 31 b-c-d), CO_3^{2-} peak is more intense due to high CO_2 content of initial $CaCO_3$.

The peak at 900 cm^{-1} and the shoulder at 860 cm^{-1} are related to bending modes of the Si–O bonds and may be attributed to La–O vibrations, whereas the peak at 640–650 cm^{-1} are attributed to Si–O and Ca–O stretching vibrations.

The peaks < 500 cm^{-1} are attributed to Si–O and Ca–O bending vibrations.

The high frequency range of glasses is characterized by a broad asymmetric band. Peaks at ~3550 cm^{-1} (Figure 32) have been identified as H_2O domain by Raman spectroscopy.

The OH–H_2O stretching domain (3000–4000 cm^{-1}) is observed in Figure 32b.

Figure 32 - a) Typical glass Raman spectra for my experiments in CSLCH system; b) High frequency range, asymmetric band of OH-H$_2$O which peaks at ~3550 cm^{-1}.

In glass spectra (Figure 31 and Figure 32), the main Raman shifts are at 1076-1078 (strong lines), confirming the dominance of carbonate in these glasses. < 300 (weak lines), 780 and 830 cm^{-1} (very weak lines).

The fundamental chemical unit of the carbonates in fact is the CO_3^{2-} anion and it is characterized by a planar trigonal geometry, where three oxygens surround the central carbon.

Glasses display a Raman peak at 1076-1078 cm^{-1} as the only significant Raman shift.

The peak is displaced relative to the main calcite peak at 1086 cm^{-1} (Figure 29c) toward lower wave numbers and is significantly broader than the calcite peak.

Both the strongest and weak peaks are similar each other within a deviation of ±1 cm^{-1}.

The presence of peaks in the range 3000–4000 cm^{-1} suggests the presence of OH-domains; in fact, the broad and asymmetric band at 3520 cm^{-1} represents molecular water and hydroxyl groups in the glass.

Figure 33 - Glasses at different SiO_2:$CaCO_3$ ratio in CSYCH.

The absence of intense bands characteristic of the carbon-hydrogen bonding in the range of 2900–3000 cm^{-1} indicates the absence of hydrocarbon bonds.

Spectral glasses ranges for CaO–SiO$_2$–Y$_2$O$_3$–H$_2$O–CO$_2$ system (CSYCH) studied at different SiO$_2$:CaCO$_3$ ratio are reported in Figure 33 in the range 100-1200 cm^{-1} shows similarities with CaO–SiO$_2$–La$_2$O$_3$–H$_2$O–CO$_2$ system, the main differences observed are different shapes at 800-1030 cm^{-1} with different SiO$_2$:CaCO$_3$ ratio and at 1500 cm^{-1} C=C (v1) (Figure 34).

Figure 34 - Example of glass in my experiments in CaO-SiO₂-Y₂O₃-H₂O-CO₂ system.

To obtain information about the structure of a glass, Nuclear Magnetic Resonance in combination with the other techniques used offers the best approach.

Y and La are considered to act as a network modifying cations in melt structures.

NMR technique can probe the local environment of a given element and is currently needed to better constrain the relationship between CO_2 molecules and REE.

In this work, the relationship between selected REE and CO_2 is analyzed at the molecular scale.

This scientific project is based on an experimental approach and state-of-the-art spectroscopic investigation. NMR analyses were performed at LPG (Nantes) and IMN Jean Rouxel (Nantes) thanks to their expertise in the field of Nuclear Magnetic Resonance spectroscopy.

We aimed to investigate simple compositions in the CaO–SiO₂–REE to limit the possible interactions between elements to obtain the fundamental relationship between 139La or 89Y and 13C through NMR spectroscopy. NMR technique is highly dependent on the element concentration so keeping a high REE concentration is a prerequisite; one of the aim is to determine the local environment in carbonatitic melts for which Ca is one of the fundamental elements.

Experimental results discussed above suggest that melts at 1 GPa, 1200°C are indeed quenchable. This is the prerequisite to investigate the network of glass structure ex-situ. At 1200°C and 1.0 GPa, run products in fact consist of CO_2-rich glass and crystalline phase (i.e., wollastonite).

NMR measurements on the samples were done in the framework of the TGIR High Field. Measurements are done in Orléans with Pierre Florian (although NMR has been done in Nantes with Michael Paris). Requirements for a better analysis were that C and La has to be reasonably concentrated so at least glasses has to get > 10 wt.% CO_2, so we investigate glasses obtained with the high content in $CaCO_3$.

Samples obtained with mostly glass and different CO_2 content had a SiO_2:$CaCO_3$ ratio of 1.4, 0.8 and 0.5. These samples have been previously characterized via EPMA, Raman and XRD (discussed above).

NMR analyses were performed for NMR35; NMR50 and NMR60 with SiO_2:$CaCO_3$ ratio of 1.4, 0.8 and 0.5 respectively. NMR samples analysis were named NMR35, NMR50 and NMR50; 35-50 and 60 represent the percentage of initial calcite in the bulk: NMR35 bulk was prepared, by inserting 13C at 50% therefore for NMR35 sample $CaCO_3$ content added contained 17.5% $CaCO_3$ and 17.5% of calcite doped in13C then 10 La_2O_3 wt.% and 55 wt.% of SiO_2.

Preliminary NMR results of La local structure show a single line with a maximum peak at ~169 ppm (Figure 35). The peak position is consistent with carbonate groups in depolymerized glass compositions and it may correspond to free ionic carbonates. It is not possible to define if the next nearest neighbor is Ca or La. NMR-35, as shown in Figure 35 has crystalline calcite hence it is tricky to get La-C relationship with this contamination.

NMR-60 is preliminary the best sample to give 13C NMR signal, showing the highest CO_2. To mimic kimberlities an additional experiment with lower SiO_2 (down to 20%) was prepared (NMR71.5 with 18.5 wt.% of SiO_2).

Figure 35 - Preliminary NMR results for NMR35-50-60 experiments.

REDOR is a method that allows probing the dipolar coupling between two elements and recorded on one of them.

In our case, the dipolar coupling between 139La and 13C is recorded on 13C.

Figure 36 - Spectra acquired for NMR 60 with REDOR method.

In Figure 36 the spectra acquired with single pulse are shown. We can clearly observe that there are two components: one at 167 and one at 169 ppm. The 169 ppm may correspond to Ca-CO_3^{2-} groups and the 167 ppm could correspond to La-CO_3^{2-}, considering that La^{3+} has higher charge. However, this is not proven.

Figure 37 - REDOR acquisition for NMR60 experiment.

Figure 37 shows the REDOR acquisitions, ideally, depending on the recoupling time in fact we should observe an increasing difference between the blue and the green curve. These results suggest that we have proximity between CO_3^{2-} and La atoms in the glass, and it can be seen thanks to the green curves or the yellow curve in Figure 36.

NMR is a selective technique and for our experiments turned out to be tricky.

These experiments have never been done before. Unfortunately, the samples are not definitive, mainly because for some of them a mixture of both crystals and glass made analysis difficult, while for others some they took a long time. For instance, acquisition on NMR60 took 2-3 days and acquisition on NMR50 tool more than 4 days, the T1 (recycle time) for 13C was in fact huge, more than 400s.

1.4 Discussion

Phase relations in REE-bearing systems, made possible the study of stability of hydrous Ca- La silicate and melting behavior in experiments on different bulk compositions. Figure 38 represents the P-T diagram with results of all experiments carried out for different $SiO_2:CaCO_3$ in $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system.

Square symbols from different colors represent calcite, quartz, Calcium-Lanthanum silicate and wollastonite phases at subsolidus conditions, while circles represent liquid and vapor phases, and triangle are the dendritic textures.

Figure 38 - After Schettino & Poli 2019 and modified adding the results of our experiments in CaO-SiO₂-La₂O₃-H₂O-CO₂ system.

Results suggest that for the investigated system no carbonate, except calcite, are stable at T between 700 and 1250°C at 1GPa. Hydrous Ca-silicates are stable at 700–800°C, at 1 GPa.

No evidence of partial melting has been found at 700 and 800°C, and the stable assemblage is made of calcite, quartz and a Ca, La silicate, at 700-800°C and 1 GPa.

Wollastonite is present at 1000°C together with quartz or calcite depending on bulk composition.

Comparing to other experimental studies performed during last decades, starting from the melting of pure calcite (Figure 38 grey line close to 1200°C, Zhao et al., 2018), the addition of Si and CO_2 lowers the solidus as demonstrated by Huang, 1980, down to a T of melting slightly lower than 700°C reported of Jones & Wyllie, 1983.

Jones & Wyllie, 1983 obtained lower solidus T in their system with the addition of H_2O (activated by Ca silicate hydrate), which further lowering and melting.

Results obtained for $CaO–SiO_2–La_2O_3–H_2O–CO_2$ (investigated from 700 to 1250°C, 1GPa) and $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ (investigated at 1250°C; 1GPa) show that solidus temperatures are higher than that observed in REE-free systems.

Some Ca-rich experiments with low $SiO_2:CaCO_3$ ratio present interstitial liquid coexisting with calcite and Ca-La or Y- phases (it depends on system investigated).

Due to the high content of initial $CaCO_3$ resulting in the low initial $SiO_2:CaCO_3 = 0.12$ ratio, $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system at 1200°C is unquenchable meanwhile at 1250°C, $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ presents interstitial glass coexistent with calcite.

Ca-La-silicate for system $CaO–SiO_2–La_2O_3–H_2O–CO_2$ and Ca-Y-silicate for system $CaO–SiO_2–Y_2O_3–H_2O–CO_2$ have been characterized by EMPA and XRD analysis. The results show that the formation of synthesized Ca-La-silicate (and probably also Ca-Y-silicate, found stable at t 1250 ° C) occurs at temperatures lower than 750°C and remains stable up to 1250°C (for selected bulk compositions with low $SiO_2:CaCO_3$ ratio). These phases found for the first time in those systems, could be compared with Dellaite phase found in $CaO–SiO_2–H_2O–CO_2$ system by Boettcher in 1969. Boettcher, as described previously in this chapter, investigated $CaO–SiO_2–H_2O–CO_2$ system, similar to one analyzed in this study but without the addition of REE elements. The stable hydrated phase found in $CaO–SiO_2–H_2O–CO_2$ system was Dellaite, silicate phases coexisting with vapor saturated fluids and liquids at HP. Dellaite, formula based on 26 ox $Ca_{12}Si_6O_{22}(OH)_4$, was identifies at T as lower of 700°C.

$CaO–SiO–La_2O_3–H_2O–CO_2$ and $CaO–SiO_2–Y_2O–H_2O–CO_2$ systems have never been investigated before. Some tests were run also by MicroRaman spectroscopy analysis (deconvolutions and peak analysis, discussed below) and preliminary by NMR analysis.

NMR analyses were performed on $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system at $SiO_2:CaCO_3 = 0.26; 0.5; 0.8$ and 1.4 ratio in order to study the local structure of La.

NMR results reveal a peak position close to ~169 ppm consistent with carbonate groups that confirms the depolymerized nature of glasses and the proximity between CO_3^{2-} and La atoms in the glass.

Experimental results for $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system, allowed at locating the liquidus for $CaO–SiO_2–La_2O_3–H_2O–CO_2$ system at temperature between 1100 and 1150°C, as it is showed in Figure 38 by the orange line.

Where starting compositions are quenched, tests show a very homogeneous glass with vapor phase evidence (e.g menisci at $SiO_2:CaCO_3 =1.4$ on DS10 experiment). Menisci indicate the presence of vapor coexisting with the liquid. Supra-liquidus conditions have been found in all bulk compositions at T > 1150°C for $SiO_2:CaCO_3$ ratio up to 0.28.

For $SiO_2:CaCO_3$ ratio lower than 0.28, in particular the bulk with $CaCO_3 = 0.12$ ratio, there is still evidence of a melt presence, therefore, we can place it in supra-liquidus conditions, but the molecular structure of the glass has a viscosity that could be not quenchable.

Experiment with $SiO_2:CaCO_3 = 0.12$ ratio shows dendritic textures. Increasing the $SiO_2:CaCO_3$ to 0.28, indeed, the viscosity is so low that the system cannot be quenched.

The limit of quenchability has been reached with SiO_2:$CaCO_3$ of 0.12, identified in these experiments as a critical point.

Thanks to these trials, we were able to identify the glass transition region, the temperature range where the intrinsic organization of melts undergoes structural changes during cooling (due to thermodynamic variable, kinetics) in a very short time intervals (few seconds to tens of minutes) (Figure 39).

Figure 39 - The glass transition in temperature-time space from Dingwell & Webb, 1990. The liquid and glass fields are defined as relaxed and unrelaxed, respectively.

The glass transition temperature (Tg), defined as temperature on the H (enthalpy)-T or Cp (Heat capacity)-T curve in the transition region during heating or cooling at a constant rate (Davies & Jones, 1953), generally defines the behavior of silicate melts into two type liquid and glassy.

Morizet et al. (2017) demonstrated by calorimeter measurements that the increase of CO_2 content induces a change in viscosity, and increasing CO_2 decreases the Tg that causes a decrease in viscosity and consequently increase of degree of polymerization.

Their work was focus on low silica melt composition (~35 wt.% SiO_2) in in the Na_2O–CaO–Al_2O_3–SiO_2 system at supra-liquidus conditions (1525°C) between 0.5 and 1.5 GPa, and it has revealed important information related to the immiscibility process between carbonate and a silicate liquids.

It is known that glass is composed of a connected and shared three-dimensional network of SiO_4 tetrahedra, with some degree of disorder in its ring structure.

The oxygens (O) linked between the Si_4 (network forming) cations are called "bridging" atoms (BO); Si-O bonds are the strongest in silicate materials. The oxides present in silicate glasses can be distinguished into network formers and network modifiers.

When alkali, alkaline earth oxide, REE or generally oxides of element with +1 or +2 valence are added to liquid silica, one oxygen bond to one SiO_4 group becoming "non-bridging" O atoms (NBO).

BO and NBO are important parameters to describe the degree of polymerization, a parameter directly associated with the composition of silicate glasses and melts. Their structure undergoes several transformations (e.g., change in viscosity or density) that depend especially on the silicon–oxygen network. The degree of polymerization can be characterized by the coefficients f = Si/O or f=T/O; the first is the ratio between the number of Si ions in the glass and the number ions of oxygen (Appen., 1974); the second is calculated when the glass contains other network forming cations (T) and it is the ratio between the sum of the numbers of ions of network forming cations (T) and the number O of gram-ions of oxygen. Network forming cations (Si-Al-Ti-Fe) form structural units linked by BO. NBO/T parameter is defined as the ratio between the number of nonbridging oxygen atoms and the total number of network formers.

In Raman spectroscopy, Si–O bending and stretching modes are influenced by the local environment: particularly, the relative intensities depend on the way in which the atoms and molecules are arranged in it (Shell, 1963). It subjected to the variation of the dipolar moment, therefore on the probability that the energetic transition from the ground state to the excited state will occur causing the absorption to the functional group.

The the molecule can vibrate in essentially two ways:

- stretching vibration due to rhythmic elongating along the binding axis, resulting in an increase and decrease in the interatomic distance;
- bending vibration due to variation of the bond angle.

Raman spectra on the glasses obtained for the investigated systems suggests a low degree of polymerization (no CO_2^{mol} has been detected), and a significant solubility of CO_2 (as CO_3^{2-}) and H_2O (Figure 40). The whole spectra can be divided into two sections: the first one comprises of the main characteristic absorption bands ranging from 400 to 1200 cm^{-1} (referred to the main silicate network group vibrations with different bonding arrangements) and the second part (especially in Figure 40b) with peaks at about 1620, 2840, 2920, and 3424 cm^{-1} (vibrations due to water, hydroxyl, or similar groups).

Figure 40 - Complete raman spectra on the range 50-3800 cm-1 on CaO-SiO$_2$-Ree-H$_2$O-CO$_2$ systems at SiO$_2$:CaCO$_3$= 0.28 a) with Lanthanum, b) with Yttrium.

The present work focus was on CO_2 dissolution; this latter plays an important role on polymerization of melts; it acts as a polymerizing agent hence increasing melt viscosity and, thus, induces a change in proportion of the different oxygen species NBO-BO.

Under oxidizing conditions in the silicate melts two species of CO_2 are dissolved: molecular CO_2 and carbonate group.

Speciation is related to the composition of the melts: CO_2 mol is dominant in polymerized and high SiO_2 glasses; CO_3^{2-} is dominant in low silica melts (as was our case).

The abundance of the CO_3 ion increases with decreasing of Si and consequently also the CO_2^{mol} decreases.

La and Y are structure modifiers: as their content increases, the structure depolymerizes; H_2O also is a structure modifier, as its dissolution as OH- creates free H+ that then bonds to bridging oxygens, breaking the tetrahedral network.

Eggler (1978) explained the effect of CO_2 on melt polymerization, suggesting that the dissolution of CO_2 as carbonate ion (CO_2^{-3}) should follow the reaction:

$$CO_2 + 2Q^n \ (M^{m+}) \rightleftharpoons CO_3^{2-}(M^{m+}) + 2Q^{n+1}$$

Where Q^n denotes a silica tetrahedron linked by bridging O atoms to n adjacent tetrahedra and M^{m+} denotes a metal cation in network modifying; the increase in polymerization is given by the building of Si–O–Si bonds.

The degree of polymerization can be represented as a function function of the Q^n species (Figure 41): Q^0 type refers to a silicon atom with zero connections to another silicon species, Q^1 type refers to a silicon atom connected to one silicon O-Si species, Q^2 type refers to a central silicon atom connected to two silicon species, Q^3 refers to a central silicon atom connected to three silicon species and Q^4 is a central silicon atom connected to four silicon species (present in pure SiO_2).

Spectral Q^n components assigned to isolated and connected SiO_4 vibrational units allow more precise analysis.

Figure 41 - Schematic diagram of the SiO4 polymerized network of a silicate glass (Colomban 2006).

Raman analysis of investigated Ca-rich low silica glasses (Figure 42) showed that spectra can be distinguished in different regions (Q^n species can be studied observing LF region), one strong polarized band at ~446 cm^{-1} assigned to Si-O-Si bending vibration mode, then a band group around ~795 cm^{-1} assigned to Si-O-Si symmetric stretching vibration of bridging oxygen between tetrahedral; a band located at 940 cm^{-1} assigned to Si-O with two nonbridging oxygens for SiO_4 tetrahedron stretching vibration (Q^2 group) and O-H region between 3550 and 3600 cm^{-1}. Peaks assignment follows Mysen (1990, 2007) and Mysen and Cody (2005).

In particular, we assigned the band at ~ 860cm^{-1} to Si–O-stretching vibrations in $Q0$-species, the band at 910 cm^{-1} to Si–O-stretching vibrations in $Q1$-species, the band at 968cm^{-1} to Si–O-stretching vibrations in $Q2$-species and the band at ~1030 cm^{-1} assigned to Si–O^0 vibration (Mysen et al., 1982). Lanthanum and Yttrium are network modifiers that may be denoted by Qn (La) and Qn (Y) located in glass structure between 950-1030 cm^{-1}. Glassy networks contain also a large amount (10%) of elements such as La or Y (it depends on experimental system investigated), which break many Si–O links glassy networks.

Generally, with addition of network modifiers, in our cases La_2O_3 or Y_2O_3, the main band shifted to lower wavenumbers and widens (Gaddam et al., 2019). We investigated two systems at fixed composition and, therefore, the shift is no evident (10 wt.% of La_2O_3 or Y_2O_3).

Figure 42 - Example of attribution of Qn species in ours spectra.

Raman spectra show the highest intensity band of the investigated glasses at 800–1200 cm^{-1} Raman shift, characteristic of structures made by isolated and poorly connected tetrahedra.

The experimental data were treated using curve-fit procedures performed by Origin-fitting and Labspec6 software.

In curve fitting, the first step was the background subtraction (baseline) from Raman raw spectra with Labspec6 program using a non-linear polynomial baseline.

Then, using the Origin program, Gaussian shape of the Raman lines was assumed because of the disordered state of examined materials. HF region was simulated with 4 gaussian peaks corresponding to the stretching vibrations of the silicate network units (Q^n) and CO_3^{2-}.

The Gaussian profile works well for solid samples, powders, gels or resins. Spectral window from 800 to 1200 cm^{-1} was used for the deconvolution of all Raman glasses spectra. The four peaks were located at 860, 950, 1030, and 1078 cm^{-1}.

At the beginning, the peak position and Full Width Half Maximum (FWHM) are kept fixed to optimize the peaks area and the four Gaussian lines the FWHM of each peak have been initially set at 50 cm^{-1}. A first set of iterations was performed to adjust the area of each Gaussian peak to give the best fit possible at this stage.

These steps are repeated several times to obtain the best $\chi2$ (chi-squared); the iteration is performed until the $\chi2$ does not change (generally the error on the peak position and FWHM is less than 1 cm^{-1}).

Solubility of CO_2 can be identified by observing molecular CO_2 or carbonate ion.

In this study, the influence of the bulk composition is expressed through initial CO_2 content. Low-silica melts can dissolve a large quantity of CO_2.

Raman spectra show the presence of CO_2 in solution mainly in the form of carbonate ion (CO_3^{2-}) with a vibrational signature peak at ~1078 cm^{-1}, indicative of a low degree of polymerization. CO_2^{mol} is absent in our spectra; molecular CO_2 is in fact not present in Si-poor glass compositions (Brooker et al., 2001b; Morizet et al., 2014).

Carbonate ion, CO_3^{2-} groups, is indeed the dominant species in lower silica or depolymerized compositions such as basaltic glasses.

In our glasses, CO_3^{2-} peak was observed at ~1074-1083 in both chemical systems.

It is evident that the addition of CO_2 modifies the shape of the Raman spectra for all investigated bulk compositions (Figure 31, Figure 33).

Glasses obtained from SiO_2:$CaCO_3$= 0.28; 0.38; 0.8; 0.5 and 1.4 at T from 1150°C to 1250°C in CaO–SiO_2–La_2O_3–CO_2–H_2O system, have been used to determinate the CO_2 solubility as carbonate ion CO_3^{2-} on Raman spectra.

For CaO–SiO_2–Y_2O_3–CO_2–H_2O system have been calculated CO_2 content in glasses with SiO_2:$CaCO_3$= 0.38; 0.5; 0.7 and 0.8 ratio at 1250°C, 1 GPa.

CO_2 solubility was determined for both systems.

In order to quantify the CO_2 dissolved into the glasses, we used the linear equation proposed by Morizet et al., (2013) which is independent on the glass composition:

$$\textbf{wt\% } CO_2 = 13.5 \times CO_3^{2-}/HF$$

where CO_3/HF is the area ratio of the fitted ν_1 carbonate peak(s) at 1062–1092 cm^{-1} to the remaining area from 800–1200 cm^{-1}.

We obtained CO_2 deconvolution with a good accuracy for our data set; peaks parameters (peak position, areas, width and Full Width Half Maximum, FWHM) were optimized until obtaining a good residual.

Residual (area with associated error) can be seen in Figure 43; it is represented as a red line following the 0 axis.

Residual close to 0 indicates a good homogeneity of glasses.

For an accurate deconvolution selection of initial input parameters are fundamental.

Figure 43 shows selected deconvolution for SiO_2:$CaCO_3$ ratio from 1.4 (Figure 43a) to 0.28 (Figure 43d), with area of CO_3^{2-} peak represented in blue. Figure 43b and Figure 43c are experiments with SiO_2:$CaCO_3$ ratio of 0.5 and differs only by temperature conditions; the experiment in Figure 43b was conducted at 1250°C, meanwhile in Figure 43c experiment was conducted at 1150°C in order to see if CO_2 content differs at different temperature. We obtained slightly higher CO_2 values for the test conducted at 1200°C.

Figure 43 - Raman spectra deconvolution for selected SiO$_2$:CaCO$_3$ ratio (1.4-0.5-0.28) in CaO-SiO$_2$-La$_2$O$_3$-CO$_2$-H$_2$O system.

Through the deconvolution made using Origin program and the peak analysis, we calculated that glasses in CSLCH system, at SiO$_2$:CaCO$_3$ ratio from 0.28 to 1.4, have CO$_2$ dissolved as carbonate within the range 2.46–20.42% (Figure 44).

Figure 44 - CO2 vs SiO2 for glasses obtained in CSLCH system.

The CO_2 behavior in silicate melt is well known, thanks to several experimental works available in literature (e.g. Blank and Brooker, 1994; Thibault and Holloway, 1994; Morizet et al., 2002). The influence of temperature on CO_2 solubility is less known contrary to what is known of its influence on pressure (CO_2 solubility increase with pressure). Blank and Brooker (1994) demonstrated that CO_2 solubility decreases with increasing temperature in rhyolite melt and increases with increasing temperature in basalt melt; it is correlated to composition (increase in alkaline melts).

Another important element is H_2O; water is probably a key parameter for the formation of carbonate melt (Genge et al., 1995; Williams and Knittle, 2003).

Ours experiments were conducted at decreasing silica content and increasing calcite content; this induces an increase in the CO_2 solubility (Brooker et al., 2001); indeed, decreasing the SiO_2 content the CO_2 solubility is above 20 wt.% in kimberlitic melts at 1.5 GPa (Moussallam et al., 2015).

Moussalam et al. (2015) investigated compositions with SiO_2 content from 25 to 32 wt.% on a volatile-free basis; starting material were mixed powders of synthetic and natural (lamproite, and calcite) materials. Experiments produced glasses without quench crystals; Raman spectra showed carbon present as carbonate ions (CO_3^{2-}) with no evidence of molecular CO_2.

The nature of the network modifying cation in the silicate melt composition is also of fundamental importance (Morizet et al., 2014, 2017a, 2019).

In glass industry, a lot of oxides have been added to products during last decades, especially in glass-ceramics industry with important applications (i.e., radomes, telescope lenses), to improve specific properties such as chemical durability, strength or translucent properties (Matusita et al., 1975; Gaddam et al., 2019).

Several trials have been done in order to investigate the effects of adding oxides of trivalent elements to silicate glasses; e.g. Y_2O_3 and La_2O_3 were added to silicate and aluminosilicate glasses.

Lanthanum oxide (La_2O_3) is an important network modifier and essential element in the glass industry. In order to understand the structural role of lanthanum ions (La3+) in silicate glasses, Gaddam et al. (2017) produced four experimental glasses with La_2O_3 content up to 4.3 mol%, Li_2CO_3 and SiO_2 at 1550°C and from spectroscopic analysis (FTIR and Raman) showed the positions of three main bands shifted to lower wavenumber values with increasing La_2O_3 contents (Figure 45).

Furthermore, at increasing of Y_2O_3 (Ebrahim & Ibrahim 2012) the positions of their main bands shifted to lower wavenumber.

Figure 45 - Raman spectra and IR of glasses. a) from Gaddam et al. (2017). La0, La1, La3 and La4 represent the molar content (0-0.9-2.6 and 4.3 mol%, respectively); b) Infrared spectra of glasses with Y_2O_3 from Ebrahim (2012).

Y_2O_3 is also an important structure modifier and as La_2O_3 it is used on glass industry and ceramics, because of its special optical properties.

We calculated spectra simulation following Morizet et al. (2013) who used four Gaussian peaks even for $CaO–SiO_2–Y_2O_3–CO_2–H_2O$ system (Figure 46).

Figure 46 - Raman spectra deconvolution for $SiO_2{:}CaCO_3$ ratio of 0.8, 0.7, 0.5 and 0.28 in $CaO{-}SiO_2{-}Y_2O_3{-}CO_2{-}H_2O$ system.

Figure 46 displays that for $SiO_2{:}CaCO_3$ ratio CO_3/Qn has the value higher than other deconvolution for experiments in the same system, as for Lanthanum system deconvolutions, we got the highest CO_3/Qn value for lower $SiO_2{:}CaCO_3$ ratio and therefore the the highest CO_2 content dissolved into ours REE glasses for lower $SiO_2{:}CaCO_3$ ratio (0.38).

This can be observed in Figure 47; deconvolution and peak analysis calculated for glasses in CSYCH system, at $SiO_2{:}CaCO_3$ ratio from 0.28 to 0.8, have CO_2 dissolved as carbonate within the range 4%–0.80%.

Figure 47 - CO₂ vs SiO₂ for glasses obtained in CSYCH system.

II) Burbankite: a REE-carbonate at high pressures

Burbankite group consists of mineral species, hexagonal or monoclinic carbonates characterized by the general formula $A_3B_3(CO_3)_5$ (Belovitskoya & Pekov, 2004).

Among all the species of the group, Burbankite is the most widespread, in fact it can be found as primary crystallizing mineral in magmatic systems (e.g. Smith et al., 2018) or mineral precipitated from alkaline solutions in lacustrine sediments (Gree River Formation in Wyoming; Fitzpatrick and Pabst, 1977) or in caves (Cioclovina cave in Romania; Onac et al., 2009).

It is also the most abundant mineral of the group; in fact, in one type of 'rare earth carbonatites' (e.g. Khibiny, Gornoe Ozero, etc), together with its alteration products, burbakite forms wide accumulations, and it potentially represents the most industrially interesting material for the extraction of REE, Sr and Ba (Belovitskoya & Pekov 2004).

2.1 State of the art

Recently, a sodium and calcium carbonate with burbankite structure has been synthesized at high pressure at 6 GPa and temperature at 1050 °C (Rashchenko et al., 2017).

The possibility to tune the chemistry of this material, as function of pressure and temperature, suggests also the possible existence of a new class of synthetic carbonates with promising non-linear optical properties (Gavryushkin et al,. 2014; Rashchenko et al., 2017).

Together with alkaline–alkaline earth fluoride carbonates (e.g. Zou et al., 2011), they can lead to an expansion of the interest of carbonates in material science.

These minerals are relevant as ore minerals, but in Earth Sciences they also might play an important role in deep carbonatitic environments as high-pressure phases which may fractionate elements from a carbonate-rich melt crystallizing at high-pressure (Shatzky et al., 2016a, b; Podbornikov et al., 2019).

Experimental investigations in the Na_2CO_3–K_2CO_3–$CaCO_3$–$MgCO_3$ systems at high pressures and temperatures has in fact revealed that above 3 GPa, new classes of Ca-rich alkaline-alkaline earth carbonates are stable and they are primary liquidus phases, with a possible important role in fractionation of deep carbonatites (Shatzky et al., 2016a, b; Podbornikov et al., 2019).

Burbankite structure was synthesized at 6 GPa and 1050 °C with chemical formula of $Na_2Ca_4(CO_3)_5$ (Rashchenko et al., 2017). These results reveal the flexibility of this structure in a wide compositional range.

Given the important role of these candidate minerals in upper mantle carbonatitic systems, and the successful synthesis of $Na_3Ca_2La\,(CO_3)_5$ at 5 GPa (Merlini et al., 2020), which proves a possible incorporation of $LREE^{3+}$ at upper mantle conditions in these carbonates,

we decided to further investigate the crystal chemical and thermoelastic properties of this phase.

The study reports the characterization and the determination of thermo-elastic properties of synthetic $Na_3Ca_2La(CO_3)_5$ at high pressure and temperature.

2.2 Experimental and analytical techniques

The synthesis of burbankite single crystals (up to 500x200x100 μm^3) was carried out at the Experimental Petrology Laboratory at the Department of Earth Sciences, University of Milan (Italy) (DES-UM) using a multi-anvil module.

Carbonate powders were mixed in stoichiometric proportions of the burbankite chemical composition. Platinum capsules with outer diameter of 3.5 mm length and 2 mm diameter were used to pack the starting composition and later welded.

The multi-anvil experiment was performed with a Cr-doped MgO octahedron of 25 mm edge length combined with tungsten carbide cubes of 32 mm truncation-edge lengths. For the experiment a graphite heater was employed, and temperatures were measured by a Pt-PtRh thermocouple (S-type). Temperature is accurate to ± 20 K, with no pressure correction for e.f.m. of thermocouple.

Pressure uncertainty was assumed ± 3% according to the accuracy of calibrant reactions (Fumagalli and Poli, 2005). Samples were synthesized at 5 GPa and 800 °C (ramp rate at about 40 K/min) with a run duration of 24 hours.

The assemblage of the recovered sample is burbankite and a Ca-rich La oxide (Figure 48).

Figure 48 – a)-b) Burbankite synthetic batch. BSE images of burbankite crystals and Ca-rich La oxide.

The two phases were well characterized via Electron Microprobe Analyses (EMPA) at the DES-UM using a Jeol 8200 electron microprobe operating at 15 nA and 15 kV. Only burbankite crystals were characterized via preliminary single crystal X-ray diffraction measurements.

The structure of the synthetic single crystal of burbankite was obtained by a single-crystal x-ray diffraction measurement at the DES-UM at room temperature using a four circles κ-

geometry Rigaku XtaLAB Synergy diffractometer. The instrument is equipped with a PhotonJet (Mo) X-ray Source, operating at 50 kV and 1 mA, with a monochromized Mo$K\alpha$ radiation, and with a Hybrid Pixel Array detector. A single crystal of ca. 100x50x50 μm^3 was picked from the experimental charge and glued on a glass fibre, which was attached on a metallic pin and mounted on a goniometer head.

During the measurements, the detector to sample distance was of 62 mm and the measurement strategy was programmed with a combination of scans in ω with 0.5° step and with an exposure time of 1.25 s at each scan step for different 2θ, κ and ϕ positions. Data reductions, including Lorenz-polarization and absorption correction based on the implemented semi-empirical ABSPACK routine, were performed using the software CrysAlisPro (Rigaku Oxford Diffraction 2019).

In-situ high-pressure (H*P*) single-crystal X-ray diffraction measurements have been carried out at the beamline Xpress of the Italian Synchrotron Elettra (Basovizza, Italy) up to ca. 7.07 GPa. A synthetic single-crystal of burbankite was loaded in a BX 90 type Diamon-Anvil Cell (DAC; Kantor et al., 2012). The pressure transmitting medium used in this experiment was a mixture of methanol: ethanol in 4:1 proportion, which transmit pressure hydrostatically up to the maximum pressure reached in this experiment (Klotz et al., 2009). Both ruby fluorescence and equation of state from single crystal of quartz were used as a pressure standard. The standard H*P* single crystal diffraction setup was used (Lotti et al., 2020), using the MAR3450 imaging plate detector with an X-ray wavelength of 0.49450 Å. In order to extract intensity suitable for structure determination, improvement in data collection protocols have been specifically designed. In particular, automatic alignment based on sample absorption assured the full illumination of the sample during the whole rotation range. The reduced rotation speed during step scans (0.25 deg/sec) and software synchronization between positioning and fast shutter operation, resulted in a significant reduction of R_{int} of integrated intensities, thus allowing a reliable structural data analysis.

The elastic behaviour of a synthetic single crystal of burbankite was characterized also by i*n-situ* high-temperature (H*T*) single crystal X-ray diffraction measurement at XRD1 beamline at the Italian Synchrotron Elettra (Basovizza, Italy). The wavelength during the experiment was 0.7000 Å and the detector used was a Pilatus 2M. A synthetic single crystal of burbankite, together with a single crystal of quartz used as standard, were loaded in a quartz-glass capillary and during the measurement crystals were kept steady with quartz-glass fibres. A hot gas blower was used to collect data every 30 °C in a temperature range from ca. 25 to ca. 470°C.

2.3 Results

Twenty points were measured on the synthetic batch of the burbankite experiment by EMPA and the composition of the points is shown in Table 1.

Table 1. Major element composition (in wt%) of the synthetic single crystals of burbankite in this study. The chemical formula has been calculated on 5 oxygens.

Na₂O	12.57	11.86	12	12.05	13.48	12.95	13.13	13.08	11.28	11.18	11.33	11.71	13.32	12.48	12.68	13.52	11.81	11.92	11.22	11.37
La₂O₃	25.15	25.43	24.88	24.4	24.93	24.58	24.82	25.14	25.19	25.95	25.82	25.85	23.97	24.44	24.79	24.1	24.77	24.35	25.71	24.69
CaO	21.45	21.59	21.99	21.88	21.53	22.05	21.47	21.35	21.9	22.12	21.93	21.41	22.24	22.35	21.81	22.2	22.09	22.54	22.1	22.45
tot	59.17	58.88	58.87	58.33	59.94	59.58	59.42	59.57	58.37	59.25	59.08	58.97	59.53	59.27	59.28	59.82	58.67	58.81	59.03	58.51
(apfu)																				
Na	2.48	2.36	2.38	2.4	2.62	2.52	2.57	2.56	2.26	2.22	2.25	2.34	2.58	2.44	2.49	2.61	2.35	2.35	2.23	2.26
La	0.94	0.96	0.94	0.93	0.92	0.91	0.93	0.94	0.96	0.98	0.98	0.98	0.88	0.91	0.93	0.88	0.94	0.91	0.97	0.93
Ca	2.34	2.38	2.41	2.41	2.31	2.37	2.33	2.31	2.43	2.42	2.41	2.36	2.38	2.42	2.37	2.37	2.42	2.46	2.43	2.47
tot	5.77	5.7	5.72	5.74	5.85	5.81	5.82	5.81	5.65	5.62	5.64	5.68	5.85	5.77	5.78	5.86	5.7	5.72	5.63	5.66
average																				
Na	2.41(13)																			
La	0.94(3)																			
Ca	2.39(5)																			

The average empirical formula calculated from the 20 analyses and based on 5 oxygens a.p.f.u. is $Na_{2.41(14)}Ca_{0.33(5)0.26}Ca_{2.06(5)}La_{0.94(3)}(CO_3)_5$. Based on the empirical formula calculated on the EMPA data, some vacancies have been evidenced.

The single crystal X-ray diffraction measurement confirms a hexagonal structure. The refined unit cell constants are $a = 10.4238(2)$; $c = 6.2910 (2)$ Å and $V = 591.97 (2)$ Å^3 at ambient conditions. The structural solution and refinement were successfully performed in the hexagonal $P6_3mc$ space group using the crystallographic software Jana2006 (Petricek et al., 2014).

The burbankite structure is characterized by the presence of two independent cationic sites, a smaller 8-fold coordinated polyhedron (A sites), a bigger 10-fold coordinated polyhedron (B sites) and three carbonate sites, which have all different orientations (Figure 49a).

Figure 49 - Crystal structure of burbankite a) projected parallel to [0 0 1] where we can observe the zigzagged 8-fold sites (yellow) and in b) we can observe the structure parallel to (0 0 1) where we can observe the 3-fold ring made of 10-fold sites(blue). The representations of the structure are realized using the program VESTA (Momma and Izumi, 2011).

The 8-fold coordination sites form infinite columns disposed at zigzag along the c-axis, where neighbouring polyhedra share their faces. The 10-fold coordination sites form also

infinite columns made of rings (composed of 3 10-fold coordination polyhedra sharing their corners) parallel to the a-c plane and in the middle of this ring a carbonate parallel to the a-b plane is laying and they share with the 10-fold sites both corners and edges. On the top of each 10-fold sites there is a carbonate group in an oblique direction. This so formed modules repeats along the c-axis but rotated by 180° (Figure 49b).

The site occupancies refinement confirms the presence of Na and Ca in the A site, and of Ca and La in the larger B site. The principal statistical parameters of the structure refinement are listed in Table 2.

Table 2. Details pertaining to the data collections and structure refinements of the burbankite studied in this work.

a (Å)	10.4238(2)
b (Å)	10.4238(2)
c (Å)	6.2910(2)
V (Å^3)	591.97(2)
Space group	$P6_3mc$
λ (Å)	0.71073
θ_{max} (°)	32.38
No. measured reflections	7382
No. unique reflections	769
No. refined parameters	54
No. restraints	0
R_{int}	0.0411
R_1 (F)	0.0296
wR_2 (F^2)	0.0366
GooF	2.03
Residuals (e$^-$/Å^3)	-2.173913043

Table 4. Lattice parameters of burbankite at different pressures, collected using methanol:ethanol (4:1) as P transmitting medium (P-uncertainty: ±0.05 GPa).

P (GPa)	a (Å)	c (Å)	V (Å^3)
0.001	10.4301(2)	6.2966(1)	593.22(2)
0.16	10.4273(3)	6.2863(7)	591.93(7)
0.54	10.4083(2)	6.2824(5)	589.41(5)
1.24	10.3727(2)	6.2561(6)	582.93(6)
2.09	10.3417(2)	6.2337(7)	577.38(6)
3.02	10.3022(2)	6.1990(8)	569.78(7)
3.7	10.2881(4)	6.165(1)	565.1(2)
5.03	10.2350(2)	6.139(1)	556.9(1)
6.06	10.2020(2)	6.109(1)	550.6(1)
6.65	10.1737(2)	6.095(1)	546.3(1)
7.07	10.1772(2)	6.079(1)	545.3(1)

Table 3. Atomic coordinates, site occupancies and equivalent displacement parameters (Å^2) of the burbankite studied in this work.

Site	x	y	z	Site occupancies	U_{eq}
A (Na, Ca)	0.52317(10)	0.04634(19)	0.379(6)	0.909(14) Na, 0.091(14) Ca	0.0171(7)
B (Ca, La)	0.84168(3)	0.68335(5)	0.691(6)	0.768(4) Ca, 0.232(4) La	0.01263(16)
C(1)	0.666667	0.33333	0.712(6)	1	0.0142(19)
C(2)	0	0	0.358(6)	1	0.0150(17)
C(3)	0.3946(5)	0.1973(2)	0.155(6)	1	0.0128(13)
O(1)	0.8092(4)	0.40462(18)	0.711(6)	1	0.0238(11)
O(2)	0.77651(18)	0.5530(4)	0.342(6)	1	0.0176(11)
O(3)	0.6322(3)	0.7093(3)	0.558(6)	1	0.0188(9)
O(4)	0.1408(4)	0.07042(18)	0.354(6)	1	0.0302(13)

Atomic coordinates and site occupancies of structure refinements are given in Table 3. Anisotropic displacement parameters and relevant bond distances are reported in Table S1, and Table S2.

The evolution of the unit-cell volume of burbankite at different pressures (P) is reported in Table 4. The volume decreases smoothly with increasing pressure, as shown in Figure 50a, up to the maximum hydrostatic pressure reached in this study of ca. 7 GPa and no phase transition or change of the deformation mechanisms occur within the P-range investigated. The P–V data were fitted using a second-order Birch–Murnaghan EoS (BM2-EoS; Birch 1947), since the Eulerian finite strain (f_e) vs. normalized stress (F_e) plot (F_e–f_e plot, Table S1) of the data can be fitted by a horizontal straight line (Angel 2000).

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
A (Na, Ca)	0.0145(8)	0.0182(10)	0.0197(10)	-0.0007(7)	-0.0003(3)	0.0091(5)
B (Ca, La)	0.01207(18)	0.0152(2)	0.0116(2)	-0.0009(3)	-0.00043(17)	0.00762(12)
C(1)	0.0178(18)	0.0178(18)	0.007(4)	0	0	0.0089(9)
C(2)	0.017(2)	0.017(2)	0.012(3)	0	0	0.0083(10)
C(3)	0.0090(16)	0.0126(12)	0.016(3)	0.0010(8)	0.0020(16)	0.0045(8)
O(1)	0.0164(14)	0.0315(13)	0.0185(19)	-0.0008(9)	-0.0017(18)	0.0082(7)
O(2)	0.0195(12)	0.0185(16)	0.0145(15)	0.0012(14)	0.0006(7)	0.0093(8)
O(3)	0.0204(11)	0.0193(11)	0.0212(11)	-0.0066(11)	-0.0033(10)	0.0134(10)
O (4)	0.0132(16)	0.0323(17)	0.039(2)	0.0016(8)	0.0033(17)	0.0066(8)

Table S1. Anisotropic displacement parameters (Å^2) of the burbankite studied in this work.

The BM2-EoS coefficients were refined simultaneously, data were weighted by their uncertainties in P and V, using the program EoSFit-7c (Angel et al., 2014) giving: V_0= 593.22(3) Å^3, K_{T0} = 69.8(4) GPa and K'=4 fixed (χ^2_w=2.04 and ΔPmax=-0.14 GPa).

Table S2. Interatomic distances (Å) selected from the structural refinement of the burbankite studied in this work.	
A -O(1)	2.3869(1)
-O(1)	2.4616(1)
-O(2)	2.3579(1)
-O(2)	2.3587(1)
-O(3)	2.3815(1)
-O(3)	2.3819(1)
-O(3)	2.7084(1)
-O(3)	2.7087(1)
$<A$ -O$>$	2.4692
B -O(1)	2.7547(1)
-O(1)	2.7551(1)
-O(2)	2.4895(1)
-O(3)	2.4776(1)
-O(3)	2.4777(1)
-O(3)	2.6011(1)
-O(3)	2.6012(1)
-O(4)	2.6494(1)
-O(4)	2.6835(1)
-O(4)	2.6839(1)
$<B$ -O$>$	2.6174
C (1)-O(1) x3	1.2871(1)
C (2)-O(4) x3	1.2715(1)
C (3)-O(2)	1.2681(1)
-O(3) x2	1.2941(1)
$<C$ (3)-O$>$	1.2854

Table 5. Lattice parameters of burbankite at different temperatures, collected in a quartz vial (T-uncertainty: ± 1 K).

T (K)	a (Å)	c (Å)	V (Å^3)
298	10.4233(2)	6.2905(1)	591.86(2)
332	10.4296(2)	6.2969(1)	593.18(2)
362	10.4353(2)	6.3022(1)	594.34(2)
391	10.4404(2)	6.3077(2)	595.44(2)
421	10.4461(2)	6.3136(2)	596.65(2)
450	10.4521(2)	6.3194(1)	597.87(2)
480	10.4581(2)	6.3252(1)	599.11(2)
509	10.4637(2)	6.3313(1)	600.34(2)
539	10.4695(2)	6.3371(1)	601.55(2)
568	10.4753(2)	6.3427(1)	602.75(2)
598	10.4839(3)	6.3478(2)	604.23(3)
628	10.4891(2)	6.3539(2)	605.41(2)
657	10.4938(3)	6.3619(2)	606.71(3)
687	10.4979(2)	6.3724(2)	608.19(3)
716	10.5016(2)	6.3856(2)	609.87(2)
746	10.5067(2)	6.3980(2)	611.66(2)

The temperature (T) – volume (V) data collected during the experiment at ambient pressure are reported in Figure 50b and Table 5.

Figure 50 - a) Evolution of the unit-cell volume with pressure of burbankite. The solid line represents the 2nd order BM-EoS fit; b) Evolution of the unit-cell volume with temperature of burbankite. Data were fitted with a Berman type EoS (solid line).

As it can be observed from Figure 50b, *V* increases continuously without any phase transition, any change of the deformation mechanisms or any evidence of an irreversible modification in the crystal during the experiment up to the maximum *T* reached in the study. The *V-T* data were fitted using EosFit 7c (Angel et al., 2014) using a Berman-type EoS (Berman 1988). The thermal expansion coefficient obtained are: α_0=6.0 (2) x 10^{-5} K^{-1}, α_1=5.7(7) x 10^{-8} K^{-2} and V_0=591.95(8) (χ^2_w=7.73).

Figure 51 - Evolution with P of the polyhedral volume for the crystal sites in the structure. a) shows the volume increase for the 8-fold coordination polyhedron, while b) are the data for the 10-folded coordination polyhedron. The black solid line represent a BM-II EoS fit to the data.

Crystal structure refinements at variable pressures indicate that the 8-fold coordination sites are more compressible than the 10-fold coordinated ones showing an inverse behavior of the two polyhedra with respect to their volume (Hazen and Finger, 1982). In fact, the smaller polyhedron is slightly more compressible with respect to the bigger one.

Table S3. Evolution with P of the V for the 8-folded and 10-folded coordinated polyhedra in burbankite structure.

P (GPa)	8-folded coordination polyhedron V (Å^3)	10-folded coordination polyhedron V (Å^3)
0.001	26.0118	38.1327
0.16	25.9677	37.9823
0.54	25.7201	37.7399
1.24	25.4523	37.4934
2.09	25.1469	37.0552
3.02	24.6685	36.6828
3.7	24.5768	36.1478
5.03	24.0418	35.9333
6.06	23.6888	35.4887
6.65	23.532	35.2665
7.07	23.4016	35.1863

(P-uncertainty: ±0.05 GPa)

Table S4. Evolution with T of the V for the 8-folded and 10-folded coordinated polyhedra in burbankite structure.

T (K)	8-folded coordination polyhedron V (Å^3)	10-folded coordination polyhedron V (Å^3)
323	25.9868	37.9708
356	26.0632	38.0622
386	26.1034	38.1461
415	26.2531	38.0354
445	26.2819	38.1681
474	26.3212	38.3796
504	26.3768	38.4898
534	26.4732	38.5476
563	26.5496	38.6021
593	26.6186	38.6775
622	26.5599	38.7516
652	26.6047	38.9862
681	26.7223	38.9477
711	26.8401	39.0045
740	26.93	39.2116
770	27.0283	39.3362

(T-uncertainty: ± 1 K)

If we try to fit the volume variation of the two polyhedra with a BM-II EoS we obtain a site K_{T0} = 54 GPa for the 8-fold coordinated polyhedra (Table S3 and Figure 51a), while for the bigger one the K_{T0} = 72 GPa (Table S3 and Figure 51b). Single crystal structure refinements at variable temperatures reveal a similar thermal expansion for both polyhedra (Figure 52 a-b and Table S4).

Figure 52 - Evolution with T of the polyhedra volume for the crystal sites in the structure. a) shows the volume increase for the 8-fold coordination polyhedron, while b) are the data for the 10-folded coordination polyhedron.

2.4 Discussion

The recent discoveries of a new class of Ca-rich alkaline-alkaline earth carbonates, including also $Ca_3(Na,K)_2(CO_3)_4$ stable above 3 GPa and primary liquidus phases in the system Na_2CO_3-K_2CO_3-$CaCO_3$ (Shatzky et al., 2016a, b; Podbornikov et al., 2019) reveal a rich and dynamic environment in carbonatite systems at high pressure.

Closer to the $CaCO_3$ end-member, bubankite-type $Na_2Ca_4(CO_3)_5$ was also synthesized (Rashchenko et al., 2017). According to experimental phase diagrams (Shatzky et al., 2016a, b; Podbornikov et al., 2019), these phases necessarily participate in crystallization and fractionation processes. Our experiments indicate that La-burbankite is still stable at 5 GPa and these candidate minerals are indeed possibly able to fractionate $LREE^{3+}$ and may form a REE reservoir in the upper mantle.

Despite its role in REE deposits and its ubiquity no studies pertaining the determination of its thermo-elastic parameters and the evolution of its structure with P and T have been published so far.

The thermo-elastic parameters determined in this study can provide a first tool to determine its density at upper mantle condition. The density of burbankite is ca. 3.2 g/cm^3 in a P and T range of 5.5 – 6 GPa and 800–1000 °C. If we compare the density of burbankite, with the density of carbonatitic magmas at the same P and T conditions, 2.058-3.1 g/cm^3 (Jones et al., 2013), we can conclude that the burbankite might fractionate from the magma and play a key role as an upper mantle reservoir of light REE^{3+}.

It is noteworth that in this example the two independent A and B polyhedra do not obey the inverse relationship (Hazen & Finger, 1982).

In this study we report a bulk modulus (K_{T0} = 72 GPa) for the 10-fold coordination site greater than the bulk modulus for the 8-fold coordination sites (K_{T0} = 54), when it is supposed to be the opposite.

It is also true that a lot of different minerals obey this relationship, with the exception of diopside (Hazen & Finger 1982). Burbankite could be another example where the inverse relationship it is not rigorously true.

Conclusions

This Ph.D work reveals important petrological results for two important issues:
Hydrous REE Low Silica Ca-rich bearing system and Thermo-elastic properties of La-burbankite carbonates.

- We investigated Carbon-bearing melt known to be difficult to quench into glasses, obtaining them from these Low Silica Ca-rich compositions represent an undoubtably important scientific result.
- Thermo-elastic properties of burbankite have revealed peculiar association with density of carbonatitic magma.

Below are summarized the main results of my PhD program.

I) The REE–CaO–SiO$_2$–H$_2$O–CO$_2$ system: the role of La and Y in the melting behavior and structure

- Liquidus condition has been observed in bulk compositions with SiO$_2$:CaCO$_3$ = 0.28-1.4 at T>1150°C for both investigated systems. Run products quenched to glasses and showed evidence of vapor phase present conditions.
- Bulk with the lowest SiO$_2$:CaCO$_3$ ratio (0.12) does not quench to glass but show typical dendritic textures.
- Glasses compositions are rather homogeneous and microprobe analyses revealed a significant number of dissolved volatiles proportional to the initial CaCO$_3$ wt.%.
- Raman spectroscopy indicated low degree of polymerization (Q^4 is not observed), and solubility of H$_2$O with typical asymmetrical appearance.
- H$_2$O and CO$_2$ are dissolved in glasses and CO$_2$ is present as carbonate ion around 1080cm-1 in both investigated systems. This intense signal confirms the very low polymerized nature from the composition calcite-rich in the case of SiO$_2$:CaCO$_3$ of 0.28, as expected.
- Following Morizet's equation, we calculated CO$_2$ content by Raman deconvolution examining 4 principal peaks, the first 4 relating to the Qn species of glass and the relating to the carbonate (CO$_2$ dissolved).
- From Raman deconvolutions we obtained for CaO–SiO$_2$–La$_2$O$_3$–CO$_2$–H$_2$O system CO$_2$ content up to 20.40% and for CaO–SiO$_2$–Y$_2$O$_3$–CO$_2$–H$_2$O system CO$_2$ content up to about 10.80%.
- CO$_2$ solubility in glasses determined by Raman spectroscopy ranges in function of initial SiO$_2$:CaCO$_3$ ratio, identifying the studied glasses as carbonate-silicate transitional melt.
- The preliminary study of molecular structure by NMR for selected bulk compositions revealed the proximity between CO$_3^{2-}$ and La atoms in the glass and the absence of CO$_2$ ^{mol} peak, confirming the depolymerized nature of the synthetic glasses obtained.

- In conclusion we were able to quench a carbon-rich melt for bulk with up to 0.28 SiO_2:$CaCO_3$ ratio.

These are the first results for those systems where indicated CO_2 solubility is what is to be expected in a carbonatititc melts.

From the experiments it emerged that there is higher T fusion compared to what is observed in systems without REE.

The results revealed a high solidus temperature and showed that Yttrium system differs from Lanthanum system in the glasses because experiments performed at the same T and P have an increase in glass transition temperatures and consequently different CO_2 solubility.

II)   The stability and mineral physics of REE-bearing carbonates, in particular of burbankite, is investigated by synthesis at 5 GPa and *in-situ* high-pressure synchrotron X-ray diffraction.

- Burbankite is an important mineral in upper mantle carbonatitic systems.
- La-burbankite $Na_3Ca_2La(CO_3)_5$ was synthesized at 5 GPa and characterized in order to determine its thermo-elastic parameters.
- The thermoelastic parameters allow us to estimate the greater density of burbankite at HP and HT.
- Density obtained from the synthesis was ca. 3.2 g/cm^3 at 5.5-6 GPa and 900–1000 °C.
- Density results directly comparable with that of carbonatitic magmas (2.058-3.1 g/cm^3).
- Results suggest that burbankite might fractionate from the magma and potentially play a key role as an upper mantle reservoir of light REE^{3+}.

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Supplementary materials

S1- Supplementary materials: Starting Bulk compositions = 1) CaO-SiO2-La2O3-H2O-CO2 ; 2) CaO-SiO2-Y2O3-H2O-CO2

1)

Content %	Bulk A	Bulk A*	Bulk B	Bulk B*	Bulk C*	Bulk D	Bulk E	Bulk F	Bulk G	Bulk H	NMR35La	NMR50La	NMR71.5La
SiO2	37.5	35	45	42.5	50	30	20	10	15	25	50	40	18.5
CaCO3	52.5	50	45	42.5	35	60	70	80	75	65	17.5	25	35.75
CaCO3 en	0	0	0	0	0	0	0	0	0	0	17.5	25	35.75
La2O3	10	0	10	0	0	10	10	10	10	10	0	10	10
La2(CO3)3	0	10	0	10	10	0	0	0	0	0	10	0	0
H2O	0	5	0	5	5	0	0	0	0	0	5	0	0

* Bulk compositions with Lanthanum Carbonate- La2(CO3)3

2)

Content %	Bulk A	Bulk B	Bulk C	Bulk D	Bulk E	Bulk F	Bulk G	Bulk H	NMR50Y
SiO2	37.5	45	55	30	15	25	20	10	40
CaCO3	52.5	45	35	60	75	65	70	80	25
CaCO3 en	0	0	0	0	0	0	0	0	25
Y2O3	10	10	10	10	10	10	10	10	10
H2O	0	0	0	0	0	0	0	0	0

CaCO3 en = Enriched in 13C

	SiO2:CaCO3 ratio
Bulk A	0.7
Bulk B	1
Bulk C	1.4
Bulk D	0.5
Bulk E	0.28
Bulk F	0.12
Bulk G	0.2
Bulk H	0.38
NMR 35La	1.4
NMR50La	0.8
NMR50Y	0.8
NMR71.5L	0.26

S2- Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS2 experiment performed at 1GPa, 700°C, SiO2:CaCO3= 0.7 . The chemical formula has been calculated on 13 oxygens.

Point analysis	DS2-22	DS2-23	DS2-24	DS2-25	DS2-26	DS2-27	DS2-28	DS2-29	DS2-30	DS2-31	DS2-34	DS2-35	DS2-36	DS2-37	DS2-38	DS2-39
SiO2	20.41	22.48	22.72	22.83	23.02	24.48	22.28	23.33	22.49	22.54	23.36	21.48	22.62	23.05	23.25	21.47
La2O3	59.62	64.48	64.73	66.95	64.54	65.1	67.13	66.17	64.82	66.62	66.06	66.19	66.49	66.65	66.14	64.32
CaO	9.42	8.96	9.33	10.4	10.09	10.47	10.25	10.29	10.29	9.59	10.49	10.17	10.17	10.51	10.61	10.96
Tot	89.45	95.92	96.78	100.18	97.65	100.05	99.66	99.79	97.6	98.75	99.91	97.84	99.28	100.21	100	96.75
(apfu)																
Si	3.16	3.24	3.24	3.16	3.23	3.31	3.13	3.22	3.18	3.18	3.21	3.09	3.16	3.18	3.20	3.09
La	3.41	3.43	3.40	3.42	3.34	3.24	3.47	3.36	3.38	3.46	3.35	3.51	3.43	3.39	3.36	3.42
Ca	1.56	1.38	1.42	1.54	1.52	1.52	1.54	1.52	1.56	1.45	1.55	1.57	1.52	1.55	1.56	1.69

S3- Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS3 experiment performed at 1GPa, 700°C, SiO2:CaCO3= 1 . The chemical formula has been calculated on 13 oxygens.

Point analysis	DS3-40	DS3-41	DS3-42	DS3-44	DS3-48	DS3-51	DS3-55	DS3-58	DS3-59	DS3-60
SiO2	22.51	21.77	23.48	23.3	22.85	22.82	22.21	20.62	22.02	21.41
La2O3	67.25	65.36	64.88	65.8	67.21	67.26	65.77	65.74	67.33	67.21
CaO	9.08	8.6	9.11	9.21	9.65	9.42	8.89	9.25	9.36	8.91
Tot	98.84	95.73	97.47	98.31	99.71	99.5	96.87	95.61	98.71	97.53
(apfu)										
Si	3.18	3.18	3.30	3.26	3.19	3.19	3.20	3.06	3.13	3.11
La	3.51	3.52	3.36	3.40	3.46	3.47	3.49	3.60	3.54	3.60
Ca	1.38	1.35	1.37	1.38	1.44	1.41	1.37	1.47	1.43	1.39

S4- Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS4 experiment performed at 1GPa, 700°C, SiO2:CaCO3= 1.4 . The chemical formula has been calculated on 13 oxygens.

Point analysis	DS4-2	DS4-4	DS4-5	DS4-7	DS4-12	DS4-63	DS4-64	DS4-66	DS4-67	DS4-68	DS4-72	DS4-77	DS4-79	DS4-83
SiO2	22.56	25.21	23.15	25.42	26.52	22.62	24.74	22.37	22.88	22.89	22.51	22.3	22.93	23
La2O3	66.81	67.6	67.74	63.91	62.1	68.37	66.71	67.29	67.99	68.62	68.11	67.05	68.51	68.78
CaO	9.52	9.75	9.63	11.25	8.87	9.18	7.38	9.01	9.29	9.1	9.98	9.27	9.87	9.55
Tot	98.89	102.56	100.52	100.58	97.49	100.17	98.83	98.67	100.16	100.61	100.6	98.62	101.31	101.33
(apfu)														
Si	3.18	3.34	3.20	3.36	3.56	3.17	3.41	3.17	3.19	3.18	3.13	3.16	3.16	3.17
La	3.47	3.30	3.45	3.12	3.07	3.53	3.39	3.52	3.49	3.52	3.50	3.51	3.48	3.50
Ca	1.44	1.38	1.43	1.59	1.27	1.38	1.09	1.37	1.39	1.36	1.49	1.41	1.46	1.41

S5 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS5 experiment performed at 1GPa, 800°C, SiO2:CaCO3= 0.7 . The chemical formula has been calculated on 13 oxygens.

Point analysis	DS5-2	DS5-15	DS5-4	DS5-3	DS5-16	DS5-8	DS5-17	DS5-5	DS5-13
SiO2	23.49	23.69	24.54	25.22	4.46	5.65	7.25	9.11	19.67
La2O3	66.23	64.2	66.93	65.75	67.64	71.12	61.39	67.38	45.24
CaO	9.81	10.24	9.64	9.52	3.69	4.18	5.89	5.72	5.16
Tot	99.53	98.13	101.11	100.49	75.79	80.95	74.53	82.21	70.07
(apfu)									
Si	3.24	3.28	3.31	3.38	1.15	1.33	1.72	1.92	3.66
La	3.37	3.28	3.33	3.25	6.45	6.19	5.37	5.24	3.10
Ca	1.45	1.52	1.39	1.37	1.02	1.06	1.50	1.29	1.03

S6 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS9.1 experiment performed at 1GPa, 1000°C, SiO2:CaCO3= 0.7 . The chemical formula has been calculated on 13 oxygens.

Point analysis	DS9.1-1.1	DS9.1-2.1	DS9.1-3.1	DS9.1-5.1	DS9.1-6.1	DS9.1-7.1	DS9.1-8.1	DS9.1-9.1	DS9.1-10.1	DS9.1-11.1	DS9.1-14.1	DS9.1-4.2	DS9.1-5.2	DS9.1-6.2	DS9.1-7.2	DS9.1-11.2	DS9.1-13.2	DS9.1-15.2
SiO2	23.53	21.72	25.87	24.1	24.97	21.82	23.17	24.83	23.13	23.7	23.31	22.87	22.97	22.83	22.92	22.45	22.9	23.06
La2O3	64.72	63.3	59.03	65.37	58.48	58.8	66.29	61.94	62.5	64.13	65.17	60.76	65.24	64.03	65.37	63.85	65.12	63.36
CaO	10.82	10.55	10.29	11.05	9.93	9.92	10.79	11.07	11.04	11.2	10.67	10.97	11.38	11.44	10.97	11.95	11.82	11.49
Tot	99.07	95.57	95.19	100.52	93.38	90.54	100.25	97.84	96.67	99.03	99.15	94.6	99.59	98.3	99.26	98.25	99.84	97.91
(apfu)																		
Si	3.24	3.15	3.52	3.26	3.49	3.27	3.18	3.37	3.24	3.25	3.22	3.26	3.17	3.18	3.18	3.14	3.15	3.21
La	3.29	3.38	2.97	3.26	3.02	3.25	3.36	3.10	3.23	3.24	3.32	3.20	3.32	3.29	3.34	3.29	3.30	3.25
Ca	1.60	1.64	1.50	1.60	1.49	1.59	1.59	1.61	1.66	1.64	1.58	1.68	1.68	1.71	1.63	1.79	1.74	1.71

S7 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS9.2 experiment performed at 1GPa, 1000°C, SiO2:CaCO3= 1 . The chemical formula has been calculated on 13 oxygens.

Point analysis	DS9.2-1.1	DS9.2-4.1	DS9.2-5.1	DS9.2-6.1	DS9.2-8.1	DS9.2-9.1	DS9.2-11.1	DS9.2-1.2	DS9.2-2.2	DS9.2-9.2	DS9.2-10.2	DS9.2-13.2	DS9.2-4.2	DS9.2-8.2	DS9.2-11	DS9.2-9	DS9.2-12	DS9.2-13
SiO2	23.28	23.45	23.34	23.32	23.46	23.32	23.51	23.58	23.39	23.14	23.46	22.93	22.66	22.65	22.46	23.14	23.39	22.93
La2O3	64.23	63.76	65.39	64.59	65.63	64.13	63.97	65.09	63.73	64.13	62.87	64.06	63.95	63.21	62.73	64.08	63.67	64.06
CaO	11	11.02	11.16	11.38	11.23	10.96	11.22	11.86	11.94	11.44	11.85	11.6	12.76	12.21	11.48	11.44	11.63	11.6
Tot	98.51	98.23	99.89	99.29	100.32	98.41	98.7	100.53	99.06	98.66	98.18	98.59	99.37	98.07	96.67	98.66	98.69	98.59
(apfu)																		
Si	3.22	3.24	3.20	3.21	3.20	3.23	3.24	3.20	3.21	3.20	3.23	3.18	3.12	3.15	3.18	3.20	3.22	3.18
La	3.28	3.25	3.31	3.27	3.30	3.28	3.25	3.26	3.22	3.27	3.19	3.28	3.25	3.25	3.27	3.27	3.23	3.28
Ca	1.63	1.63	1.64	1.68	1.64	1.63	1.65	1.72	1.75	1.70	1.75	1.72	1.88	1.82	1.74	1.70	1.71	1.72

S8 Major element composition (in wt.%) of Calcium–Lanthanum silicate from DS9.3 experiment performed at 1GPa, 1000°C, SiO2:CaCO3= 1.4. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS9.3-1 .1	DS9.3-4 .1	DS9.3-15 .2	DS9.3-16 .2	DS9.3-17 .2	DS9.3-18 .2	DS9.3-19 .2	DS9.3-12 .2
SiO2	23.46	23.19	22.94	23.29	23.69	23.28	22.95	23.25
La2O3	63.37	63.52	63.61	66.22	64.37	64.07	64.68	64.81
CaO	11.11	11.57	12.15	11.99	12.43	11.68	12.24	12.14
Tot	97.94	98.2801	98.7	101.5	100.49	99.03	99.87	100.2
(apfu)								
Si	3.25	3.21	3.17	3.15	3.20	3.20	3.15	3.17
La	3.24	3.24	3.24	3.31	3.20	3.25	3.27	3.26
Ca	1.65	1.72	1.80	1.74	1.80	1.72	1.80	1.77

S9 Major element composition (in wt.%) of Calcium–Lanthanum silicate from DS11 experiment performed at 1GPa, 800°C, SiO2:CaCO3= 0.5. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS11-1	DS11-2	DS11-3	DS11-4	DS11-5	DS11-6	DS11-7
SiO2	23.28	23.59	23.29	23.84	24.41	22.96	22.53
La2O3	67.52	66.83	68.01	67.28	66.37	67.8	67.79
CaO	9.72	9.64	9.62	10.1	9.61	10.04	9.84
Total	100.52	100.06	100.92	101.22	100.39	100.8	100.16
(apfu)							
Si	3.21	3.25	3.20	3.24	3.31	3.17	3.15
La	3.43	3.39	3.45	3.37	3.32	3.45	3.49
Ca	1.44	1.42	1.42	1.47	1.40	1.48	1.47

S10 Major element composition (in wt.%) of Calcium–Lanthanum silicate from DS12 experiment performed at 1GPa, 900°C, SiO2:CaCO3= 0.5. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS12-1	DS12-2	DS12-3	DS12-4	DS12-5	DS12-6	DS12-7
SiO2	24.26	23.68	26.1	25.7	27.3	22.98	25.04
La2O3	62.82	63.27	61.06	61.94	62.5	62.99	62.12
CaO	11.71	11.63	12.39	11.85	11.33	11.45	11.45
Total	99.13	98.58	99.55	100.01	101.58	98.02	98.61
(apfu)							
Si	3.29	3.25	3.42	3.40	3.50	3.21	3.37
La	3.14	3.20	2.95	3.02	2.96	3.24	3.08
Ca	1.70	1.71	1.74	1.68	1.56	1.71	1.65

S11 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS13 experiment performed at 1GPa, 700°C, SiO2:CaCO3= 0.5. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS13-1	DS13-3	DS13-4	DS13-7	DS13-8	DS13-9	DS13-10
SiO2	21.56	22.51	22.82	23.39	24.45	23.47	22.83
La2O3	65.7	62.68	57.56	63.09	63.13	67.06	67.45
CaO	9.59	11.53	9.74	12.12	9.67	11.04	9.43
Total	97.36	96.72	90.12	98.71	97.25	101.57	99.88
(apfu)							
Si	3.12	3.18	3.37	3.21	3.37	3.18	3.19
La	3.51	3.26	3.14	3.20	3.21	3.35	3.47
Ca	1.49	1.74	1.54	1.78	1.43	1.60	1.41

S12 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS14 experiment performed at 1GPa, 1200°C, SiO2:CaCO3= 0.5. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS14-21	DS14-22	DS14-23	DS14-24	DS14-16
SiO2	23.52	23.33	23.42	23.6	23.93
La2O3	61.53	60.62	60.9	61.07	61.87
CaO	13.28	12.81	13.15	13.3	13.74
Total	98.33	96.76	97.47	97.97	99.54
(apfu)					
Si	3.21	3.23	3.22	3.22	3.21
La	3.10	3.09	3.09	3.07	3.06
Ca	1.94	1.90	1.94	1.95	1.98

S13 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS16 experiment performed at 1GPa, 1100°C, SiO2:CaCO3= 0.5. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS16-1	DS16-2	DS16-3	DS16-4	DS16-5	DS16-6	DS16-7	DS16-8	DS16-9	DS16-10	DS16-13	DS16-14	DS16-15	DS16-16	DS16-17	DS16-18	DS16-19	DS16-20	DS16-21	DS16-22
SiO2	22.53	22.4	23.76	23.66	23.23	22.74	23.34	24.22	21.82	21.39	22.71	23.36	20.78	22.54	24.15	23.9	22.74	23.36	24.13	23.47
La2O3	62.34	63.04	62.73	63.27	63.1	61.42	62.31	61.51	60.95	62.49	61.47	60.64	59.73	60.86	62.14	62.53	61.19	61.98	62.14	62.01
CaO	11.32	11.69	11.59	11.59	11.93	12.1	12.06	12.01	11.89	11.74	11.75	12.49	11.65	11.76	11.55	12.02	12.43	12.22	12.16	12.02
Total	96.19	97.13	98.08	98.52	98.26	96.26	97.71	97.74	94.66	95.62	95.93	96.49	92.16	95.16	97.84	98.45	96.36	97.56	98.43	97.50
(apfu)																				
Si	3.19	3.16	3.26	3.25	3.21	3.20	3.23	3.30	3.15	3.09	3.21	3.24	3.10	3.21	3.30	3.26	3.19	3.23	3.28	3.24
La	3.26	3.28	3.18	3.20	3.21	3.19	3.18	3.09	3.24	3.33	3.20	3.10	3.29	3.19	3.13	3.15	3.17	3.16	3.11	3.16
Ca	1.72	1.77	1.71	1.70	1.76	1.82	1.79	1.75	1.84	1.82	1.78	1.86	1.86	1.79	1.69	1.76	1.87	1.81	1.77	1.78

S14 Major element composition (in wt.%) of Calcium-Lanthanum silicate from DS20 and NMR71.5 experiments performed at 1GPa, 1100°C and 1250°C, SiO2:CaCO3= 0.5 and 0.26. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS20-1	DS20-2	DS20-3	DS20-5	DS20-6	DS20-25	NMR71-1	NMR71-2	NMR71-3	NMR71-4	NMR71-5
SiO2	24.74	25.9	25.71	14.76	19.43	24.03	23.86	23.76	23.72	23.8	23.68
La2O3	62.92	62.91	62.42	58.29	58.42	62.11	57.76	60.62	59.38	58.2	58.28
CaO	8.99	8.83	9.73	7.11	6.77	13	14.5	12.72	13.47	14.41	14.68
Total	96.65	97.64	97.86	80.16	84.62	99.14	96.12	97.1	96.57	96.41	96.64
(apfu)											
Si	3.42	3.51	3.47	2.77	3.22	3.24	3.26	3.26	3.26	3.25	3.23
La	3.21	3.14	3.11	4.03	3.57	3.09	2.91	3.07	3.01	2.93	2.93
Ca	1.33	1.28	1.41	1.43	1.20	1.88	2.12	1.87	1.98	2.11	2.14

S15 Major element composition (in wt.%) of Calcium-Yttrium silicate from DS26-27-28-29 experiments performed at 1GPa, 1250°C, SiO2:CaCO3= 0.5-0.28-0.12-0.7. The chemical formula has been calculated on 13 oxygens.

Point analysis	DS26-1	DS26-2	DS26-3	DS27-4	DS27-5	DS27-6	DS28-4	DS28-7	DS28-10	DS28-11	DS28-12	DS29-4	DS29-7
SiO2	28.05	28.74	28.01	28.49	28.21	28.16	27.45	27.63	28.15	27.63	27.86	27.86	28.26
CaO	16.5	22.88	16.46	16.07	16.19	16.07	16.98	16.96	16.02	15.92	15.82	16.22	16.22
Y2O3	53.2	45.11	53.21	53.03	53.45	53.31	52.4	53.24	53.91	53.99	53.69	53.01	52.99
Total	97.75	96.73	97.73	97.78	97.85	97.54	96.83	97.93	98.08	97.54	97.37	97.09	97.57
(apfu)													
Si	2.30	2.80	2.30	3.18	3.15	3.15	3.11	3.10	3.14	3.11	3.14	3.14	3.16
Y	3.95	2.94	3.96	3.15	3.18	3.18	3.15	3.18	3.20	3.24	3.22	3.18	3.15
Ca	2.47	3.00	2.46	1.92	1.94	1.93	2.06	2.04	1.92	1.92	1.91	1.96	1.94

S16- GLASS- Major element composition (in wt.%) of Glass from DS10 experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 1.4.

Point analysis	DS10-2	DS10-3	DS10-10	DS10-11	DS10-12	DS10-1	DS10-2	DS10-3	DS10-4	DS10-5	DS10-6	DS10-7	DS10-8	DS10-9	DS10-10	DS10-11	DS10-12	DS10-13	DS10-14	DS10-15
SiO2	56.22	59.03	58.44	58.93	58.86	58.87	59.4	59.6	59.23	59.46	59.18	59.57	59.13	59.76	59.04	59.54	59.5	59.38	59.25	59.27
La2O3	9.57	9.36	9.29	9.21	9.15	8.92	8.88	8.85	8.98	8.97	8.97	9.08	9.09	9.15	8.95	8.86	9.22	8.88	8.96	8.86
CaO	25.38	24.41	24.43	23.98	23.98	24.09	24.18	24.33	24.11	24.23	24.09	24.38	24.2	23.99	24.24	24.31	24.09	24.15	24.23	24.35
Total	91.17	92.87	92.16	93.01	92.11	91.88	92.46	92.78	92.32	92.66	92.24	93.03	92.42	92.90	92.23	92.71	92.81	92.41	92.44	92.48

Major element composition (in wt.%) of Glass from DS14 experiment performed at 1GPa, 1200°C, SiO2:CaCO3= 0.5.

Point analysis	DS14-6	DS14-7	DS14-8	DS14-9	DS14-10	DS14-11	DS14-12	DS14-13	DS14-14	DS14-15	DS14-26	DS14-27	DS14-28	DS14-29	DS14-30	DS14-31	DS14-32	DS14-17
SiO2	29.47	29.71	29.79	29.44	29.87	29.72	29.56	29.65	29.59	29.43	32.26	31.47	30.72	31.88	31.89	32.37	33.39	15.84
La2O3	11.06	11.21	11.63	11.01	11.01	11.2	11.11	11.73	11.45	11.54	11.47	10.98	11.3	11.27	10.95	10.78	11.09	29.94
CaO	41.26	40.84	41.17	41.2	41.35	41.34	41.37	41.23	41.11	41.24	37.93	38.17	37.58	37.74	38.33	37.8	37.9	34.42
Total	81.79	81.76	82.59	81.65	82.23	82.26	82.04	82.61	82.15	82.21	81.66	80.62	79.60	80.89	81.17	80.95	82.38	80.20

Major element composition (in wt.%) of Glass from DS17 experiment performed at 1GPa, 1150°C, SiO2:CaCO3= 0.5.

Point analysis	DS17-4	DS17-5	DS17-6	DS17-7	DS17-8	DS17-9	DS17-10	DS17-11	DS17-12	DS17-13	DS17-1	DS17-2	DS17-3	DS17-19	DS17-20
SiO2	33	29.73	30.33	32.68	32.95	32.66	30.86	31.06	32.63	32.3	33.71	34.02	34.39	33.63	34.38
La2O3	10.26	9.82	9.56	10.06	10.58	10.29	10.18	10.07	10.08	10.49	8.15	8.68	7.6	7.87	7.58
CaO	39.58	37.68	38.17	39.69	39.54	39.55	39.16	39.2	39.64	39.49	39.07	38.72	39.01	39.1	37.85
Total	82.84	77.23	78.06	82.43	83.07	82.50	80.20	80.33	82.35	82.28	80.93	81.42	81.00	80.60	79.81

S17 - GLASS- Major element composition (in wt.%) of Glass from DS18 experiment performed at 1GPa, 1200°C, SiO2:CaCO3= 0.28.

Point analysis	DS18-10	DS18-11	DS18-12	DS18-13	DS18-14	DS18-15	DS18-16	DS18-17	DS18-18	DS18-19	DS18-20	DS18-21	DS18-22	DS18-23	DS18-24	DS18-25
SiO2	21.24	20.83	20.57	20.62	20.39	20.66	19.8	18.98	19.48	20.39	20.5	19.23	19.51	19.57	23.03	22.35
La2O3	9.44	8.81	9.49	9.12	9.05	9.06	8.6	8.3	8.67	9.1	9.09	8.32	8.35	8.84	12.28	12.93
CaO	43.94	43.97	43.82	43.8	42.48	43.29	42.45	42.52	42.56	42.98	42.85	42.61	42.39	42.44	45.46	46.73
Total	74.62	73.61	73.88	73.54	71.92	73.01	70.85	69.8	70.71	72.47	72.44	70.16	70.25	70.85	80.77	82.01

GLASS- Major element composition (in wt.%) of Glass from NMR35 experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 1.57.

Point analysis	NMR35-GL1	NMR35-GL2	NMR35-GL3	NMR35-GL4	NMR35-GL5	NMR35-GL6	NMR35-GL7	NMR35-GL8	NMR35-GL9	NMR35-GL10	NMR35-GL11	NMR35-GL12	NMR35-GLB1	NMR35-GLB2	NMR35-GLB3	NMR35-GLB4
SiO2	54.32	54.29	54.03	54.16	53.84	53.67	53.63	53.44	53.65	53.27	52.73	53.39	54.19	53.77	53.8	53.51
La2O3	12.38	12.53	12.68	12.94	12.99	12.77	13.13	12.98	12.89	12.88	12.75	12.66	12.99	12.77	12.66	12.7
CaO	29.33	29.67	29.5	29.52	29.91	29.39	29.8	29.68	29.87	30.06	30.54	30.1	29.65	29.7	29.87	30.11
Total	96.03	96.49	96.21	96.62	96.74	95.83	96.56	96.1	96.41	96.21	96.02	96.15	96.83	96.24	96.33	96.32

Point analysis	NMR35-GLB5	NMR35-GLB6	NMR35-GLB7	NMR35-GLB8	NMR35-GLB9	NMR35-GLB10	NMR35-GLB11	NMR35-GLB12	NMR35-GLB13	NMR35-GLB14	NMR35-GLB15	NMR35-GLB16	NMR35-GLB17	NMR35-GLB18	NMR35-GLB19
SiO2	53.15	53.47	53.29	53.42	52.68	52.87	52.1	52.3	52.73	52.58	52.96	52.95	53.02	53.23	52.45
La2O3	12.67	12.86	12.82	13.31	12.74	12.72	12.63	12.86	12.61	12.65	12.78	12.63	12.33	12.88	12.92
CaO	29.88	29.87	29.98	29.85	30.19	29.94	30.27	30.24	30.06	30.11	30.06	30.05	30.31	29.8	30.58
Total	95.7	96.2	96.09	96.58	95.61	95.53	95	95.4	95.4	95.34	95.8	95.63	95.66	95.91	95.95

S18- GLASS- Major element composition (in wt.%) of Glass from NMR50La experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 0.8.

Point analysis	NMR50-GL1	NMR50-GL2	NMR50-GL3	NMR50-GL4	NMR50-GL5	NMR50-GL6	NMR50-GL7	NMR50-GL8	NMR50-GL9	NMR50-GL10	NMR50-GL11	NMR50-GL12	NMR50-GL13	NMR50-GL14	NMR50-GL15	NMR50-GL16	NMR50-GL17	NMR50-GL18	NMR50-GL19
SiO_2	43.61	43.78	44.37	44.15	44.12	44.16	43.91	44.29	44.27	44.04	36.73	43.73	44.19	43.22	39.38	42.92	38.53	43.35	40.3
La_2O_3	9.16	9.38	9.29	9.47	9.45	9.19	9.52	9.6	9.52	9.47	7.79	9.06	9.59	9.69	8.87	9.44	8.48	9.45	8.91
CaO	30.78	30.4	30.66	30.69	30.95	31.11	31.47	31.28	31.25	31.11	26.1	30.82	31.07	31.24	28.94	31	29.11	31.22	29.93
Total	83.55	83.56	84.32	84.31	84.52	84.46	84.9	85.17	85.04	84.62	70.62	83.61	84.85	84.15	77.19	83.36	76.12	84.02	79.14

GLASS- Major element composition (in wt.%) of Glass from DS21 experiment performed at 1GPa, 1200°C, SiO2:CaCO3= 0.20.

Point analysis	DS21-GL1	DS21-GL2	DS21-GL3	DS21-GL4	DS21-GL5	DS21-GL6	DS21-GL7	DS21-GL8	DS21-GL9	DS21-GL10
SiO_2	16.23	18.14	18.27	15.25	21.45	18.9	16.51	16.34	21.75	26.55
La_2O_3	9.58	9.46	9.48	8.39	8.21	8.92	8.27	7.76	2	6.55
CaO	45.72	45.03	45.02	48.53	41	45.09	46.23	47.27	12.78	29.44
Total	71.53	72.63	72.77	72.17	70.66	72.91	71.01	71.37	36.53	62.54

GLASS- Major element composition (in wt.%) of Glass from DS23 experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 0.38.

Point analysis	DS23-GL1	DS23-GL2	DS23-GL3	DS23-GL4	DS23-GL5	DS23-GL6	DS23-GL7	DS23-GL8	DS23-GL9	DS23-GL10	DS23-GL11	DS23-GL12	DS23-GL13	DS23-GL14	DS23-GL15
SiO_2	29.69	30.28	29.81	31.1	30.4	30.1	32.12	30.7	30.9	30.18	31.74	29.91	30.96	30.07	29.57
La_2O_3	10.19	10.03	10.15	10.26	9.77	9.77	9.88	9.67	9.59	9.59	9.99	9.37	9.57	9.54	9.63
CaO	41.78	42.03	41.11	40.69	39.57	39.53	39.08	39	38.56	39.12	38.97	37.76	38.57	38.6	38.33
Total	81.66	82.34	81.07	82.05	79.74	79.4	81.08	79.37	79.05	78.89	80.7	77.04	79.1	78.21	77.53

S19- GLASS- Major element composition (in wt.%) of Glass from DS24 experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 1.

Point analysis	DS24-GL1	DS24-GL2	DS24-GL3	DS24-GL4	DS24-GL5	DS24-GL6	DS24-GL7	DS24-GL8	DS24-GL9	DS24-GL10	DS24-GL11	DS24-GL12	DS24-GL13	DS24-GL14
SiO2	53.58	53.28	53.63	53.78	53.88	53.56	53.35	53.09	52.54	52.8	52.74	52.94	53.03	51.86
La2O3	9.98	10.28	10.18	10.58	10.38	10.56	10.56	10.61	10.3	10.54	10.41	10.46	10.38	10.12
CaO	30.58	30.46	30.64	30.59	30.77	30.66	30.85	30.93	30.79	30.91	30.86	30.87	30.54	29.99
Total	94.14	94.02	94.45	94.95	95.03	94.78	94.76	94.63	93.63	94.25	94.01	94.27	93.95	91.97

GLASS- Major element composition (in wt.%) of Glass from DS25 experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 0.7.

Point analysis	DS25-GL2	DS25-GL3	DS25-GL4	DS25-GL5	DS25-GL6	DS25-GL7	DS25-GL8	DS25-GL9	DS25-GL10	DS25-GL11	DS25-GL12	DS25-GL13	DS25-GL14	DS25-GL15
SiO2	46.6	46.07	46.05	46.4	46.1	45.98	46.44	46.32	46.75	45.53	45.91	45.53	45.64	45.13
La2O3	10.36	10.16	9.99	10.04	10.24	10.13	10.06	10.27	9.95	10.08	10.29	10.17	10.26	9.95
CaO	34	34.16	34.14	34.07	34.2	34.04	34.01	34.21	34.29	34.23	34.13	34.37	34.36	33.94
Total	90.96	90.39	90.18	90.51	90.54	90.15	90.51	90.8	90.99	89.84	90.33	90.07	90.26	89.02

GLASS- Major element composition (in wt.%) of Glass from NMR60La experiment performed at 1GPa, 1150°C, SiO2:CaCO3= 0.5.

Point analysis	NMR60-GL1	NMR60-GL2	NMR60-GL3	NMR60-GL4	NMR60-GL5	NMR60-GL6	NMR60-GL7	NMR60-GL8	NMR60-GL9	NMR60-GL10	NMR60-GL11	NMR60-GL12
SiO2	31.89	32.09	32.14	32.2	25.08	32.07	33.78	33.17	34.05	33.34	33.17	28.22
La2O3	9.37	9.67	9.79	9.55	7.47	9.41	9.79	9.46	9.81	9.37	9.57	8.67
CaO	38.81	39.16	39.51	38.4	31.51	38.36	38.45	38.67	38.45	37.65	37.37	35.13
Total	80.07	80.92	81.44	80.15	64.06	79.84	82.02	81.3	82.31	80.36	80.11	72.02

S20- GLASS- Major element composition (in wt.%) of Glass from DS26 experiment performed at 1GPa ,1250°C, SiO2:CaCO3= 0.5.

Point analysis	DS26-5	DS26-6	DS26-7	DS26-8	DS26-9	DS26-10	DS26-11	DS26-12	DS26-13	DS26-14
SiO2	33.56	33.81	33.57	33.41	33.54	33.06	33.59	33.64	33.38	33.77
CaO	42.34	42.18	42.2	42.3	42.44	41.98	42.18	42.08	42.08	42.28
Y2O3	8.5	8.48	8.41	8.47	8.51	8.02	8.33	8.42	8.59	8.45
Total	84.41	84.47	84.24	84.18	84.49	83.06	84.10	84.14	84.12	84.52

GLASS- Major element composition (in wt.%) of Glass from DS27 experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 0.28.

Point analysis	DS27-10	DS27-11	DS27-12	DS27-13	DS27-14	DS27-15	DS27-16	DS27-17	DS27-18	DS27-19
SiO2	19.23	19.4	19.1	19.02	19.19	19.16	19.15	19.34	19.24	19.42
CaO	46.95	47.34	47.35	47.21	47.37	46.34	46.46	47.29	47.53	47.95
Y2O3	6.05	6.42	6.22	6.57	6.33	6.11	6.47	6.39	5.88	6.16
Total	72.23	73.16	72.67	72.80	72.92	71.65	72.20	73.02	72.65	73.55

GLASS- Major element composition (in wt.%) of Glass from NMR50Y experiment performed at 1GPa, 1250°C, SiO2:CaCO3= 0.8.

Point analysis	YNMR50-GLX1	YNMR50-GLX2	YNMR50-GLX3	YNMR50-GLX4	YNMR50-GLX5	YNMR50-GLX6	YNMR50-GLX7	YNMR50-GLX8	YNMR50-GLX9	YNMR50-GLX10	YNMR50-GLX11	YNMR50-GLX12	YNMR50-GLX13	YNMR50-GLX14	YNMR50-GLX15	YNMR50-GLX16	YNMR50-GLX17	YNMR50-GLX18	YNMR50-GLX19	YNMR50-GLX20
SiO2	45.69	46.15	46.4	46.41	46.52	45.88	44.67	46.12	46.01	46.25	46.14	45.96	45.7	45.97	45.75	45.44	45.72	45.86	45.83	46.31
Y2O3	6.34	6.61	6.67	6.61	6.52	6.48	6.45	6.54	6.57	6.67	6.7	6.42	6.41	6.42	6.46	6.33	6.51	6.45	6.45	6.6
CaO	33.66	34.36	34.12	34.15	34.26	34.3	33.21	34.34	33.91	34.28	34.23	34.17	34.08	34.41	34.28	34.28	34.02	34.06	34.4	34.13
Total	85.74	87.12	87.24	87.19	87.32	86.72	84.33	87.00	86.62	87.21	87.08	86.66	86.19	86.85	86.56	86.05	86.25	86.44	86.72	87.04

Point analysis	YNMR50-GL1	YNMR50-GL2	YNMR50-GL3	YNMR50-GL4	YNMR50-GL5	YNMR50-GL6	YNMR50-GL7	YNMR50-GL8	YNMR50-GL9	YNMR50-GL10	YNMR50-GL11	YNMR50-GL12	YNMR50-GL13	YNMR50-GL14	YNMR50-GL15	YNMR50-GL16	YNMR50-GL17	YNMR50-GL18	YNMR50-GL19	YNMR50-GL20
SiO2	47.46	47	47.06	46.83	46.77	46.75	47.01	47.05	46.53	47.12	39.87	39.7	46.27	46.65	46.52	44.98	46.23	46.52	46.71	46.71
Y2O3	6.62	6.58	6.62	6.56	6.63	6.7	6.79	6.45	6.74	6.88	5.74	5.51	6.46	6.85	6.73	6.16	6.5	6.65	6.7	6.76
CaO	33.94	33.97	34.05	33.87	34.02	34.16	33.83	34.06	33.82	33.9	28.96	28.33	33.97	34.07	34.1	33.01	33.76	33.98	34.1	34.19
Total	88.02	87.70	87.75	87.26	87.51	87.66	87.67	87.56	87.14	87.91	74.59	73.54	86.80	87.57	87.43	84.25	86.57	87.15	87.53	87.66